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A Simple Synthetic Access to Differently 4-Substituted Neu5Ac2en Glycals Combining Elements of Molecules with Anti-Neuraminidase Activity

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A protocol for direct access to C-4-functionalized Neu5Ac2en derivatives by allylic substitution of an α-acetoxy group with various nucleophiles is reported. The DANA acetamido group is exchanged for a trifluoroacetylamido group (as in FANA) to avoid the formation of a stable 4,5-oxazoline. With thiols, the reaction involves an initial attack at the anomeric carbon (Ferrier reaction) under kinetic control, followed by an equilibration of the nucleophile to the thermodynamically more stable 4-position.

Introduction

Various glycals of *N*-acetylated neuraminic acid **1** (Neu5Ac; Figure 1), such as, for example, 5-acetamido-2,6-anhydro-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-enoic acid **2a** (Neu5Ac2en, DANA),[1–5] its 5-perfluoroacetylated analogue **2b** (FANA),[6] and the 4-deoxy-4-guanidino congeners of DANA (i.e., Zanamivir, **2c**)[1–3,7] and of FANA (i.e., **2d**),[8] are potent inhibitors of sialidases (neuraminidases, NA). Sialidases are important surface glycoproteins of bacterial and viral membranes that play crucial roles in the spreading of infection to new host cells.[3,7,8] For this reason, much effort has been put into the preparation of various DANA and FANA congeners substituted at C-4, as possible NA inhibitors.[1,5,6–11]

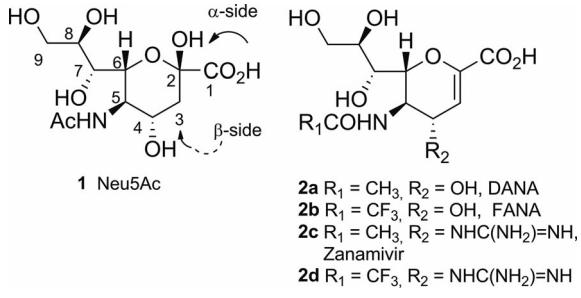

Figure 1. Structures of Neu5Ac and its glycals.

As a part of our research into C-4-substituted sialic acid glycals combining elements of molecules with anti-NA activity, we have recently reported[12,13] a simple synthetic strategy for the transformation of DANA and FANA glycals **3** and **4** into the 4β-acylamidated FANA and DANA glycals, by a Ritter reaction (Scheme 1).[14] To achieve this, we reversibly transformed peracetylated DANA ester **3**[15] into peracetylated FANA methyl ester **4**[16] to avoid the intramolecular β-attack of the 5-acetamido group onto the adjacent 4-position of the DANA glycal, which would inevitably form stable oxazoline[17] **5** (Scheme 1). This allowed a Ritter reaction to take place to give 4β-acetamido derivative **6b**, which could be transformed into DANA analogue glycal **7**, by a simple and selective exchange of its 5β-acylamido group (Scheme 1).

Continuing our interest in NA inhibitors, we searched for a possible extension of the aforementioned Ritter reaction that could be used to insert many other different groups at the 4-position of a fluorinated Neu5Ac glycal. In this paper, we report the successful results obtained with a variety of nucleophiles together with a possible rationalization of the regio- and stereochemical outcomes of the reaction. For thiol nucleophiles, this involved a Ferrier reaction,[18] a rearrangement that has been almost completely ignored in sialic acid glycal chemistry, apart from a study by K. Ikeda et al. on sialic acid 4,5-oxazoline **5**.[19]

Results and Discussion

Initially, we verified that our Ritter reaction could be performed using acetonitrile as a reagent, in a different solvent, and in the presence of a Lewis acid promoter. In preliminary experiments, we obtained encouraging results with $BF_3{\cdot}Et_2O$ and with TMSOTf (TMS = trimethylsilyl), operating at 40 °C in dichloromethane or nitromethane

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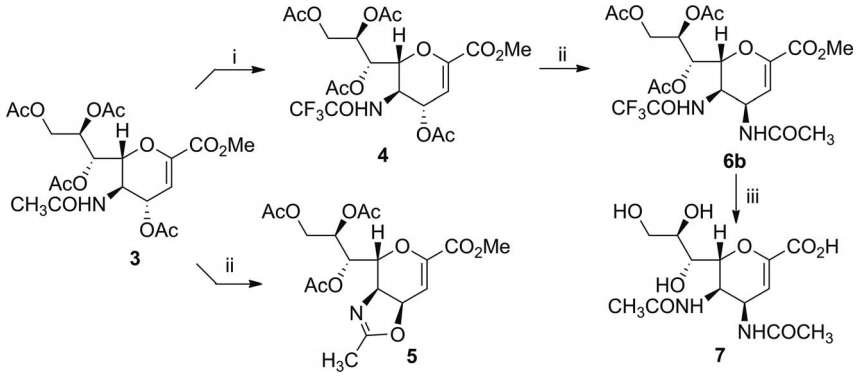
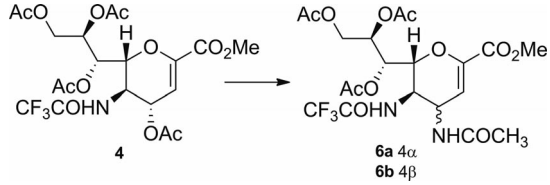


Scheme 1. Avoidance of oxazoline formation, and 4β-acetamidation of Neu5Ac glycals by a Ritter reaction. *Reagents and conditions:* (i) $(CF_3CO)_2O$, CH_3CN, 135 °C, 15 min; (ii) CH_3CN, H_2SO_4, 50 °C, 30 min; (iii) K_2CO_3, MeOH (aq.), 23 °C, 12 h, then CH_3COCl, MeOH (aq.), 23 °C, 30 min.

(Table 1). Under the best-found conditions, glycals **6a** and **6b** were formed in satisfactory yields and in very short reaction times (Table 1, entries 1, 2, and 7), although a decrease in the β-stereoselectivity was observed compared to the reactions where acetonitrile was used as the solvent (α/β = 2:3 rather than α/β = 0:10).[12,13] The stereoselectivity was not improved by varying the reaction conditions (temperature, solvent, Lewis acid, amount of reagent, etc.; Table 1, entries 3–6, 8, and 9), or even by using H_2SO_4, the typical protic acid catalyst of the Ritter reaction[14] (Table 1, entries 10 and 11). Since under milder conditions (lower temperature and less of the Lewis acid), the reaction appeared to take too long without any improvement of the stereoselectivity, we decided to perform our reaction at 40 °C, a temperature that would give convenient reaction times, using $BF_3{\cdot}Et_2O$ (10 equiv.) as promoter and dichloromethane as solvent. Under these conditions, the reaction worked satisfactory with several nucleophiles (Table 2), including sulfonamides (Table 2, entries 1–3), simple and less simple primary and secondary alcohols (Table 2, entries 4–10), substituted phenols (Table 2, entries 13–14), thiols, thiophenols, and amino acidic thiols (Table 2, entries 15–18), hydrides (Table 2, entry 19), and halogen ions (Table 2, entries 20–21). The results were poor only with tertiary alcohols and simple phenols (Table 2, entries 11–12). In all the successful cases, the formation of a 4-substituted glycal was observed, apart from the reactions with cysteine and triethylsilane (TESH), where an S_N2-like reaction was observed with a shift of the double bond to give 2-substituted α glycosides **23a** and **24a**, respectively (Table 2, entries 18 and 19). Such a reaction, known as a Ferrier rearrangement, has been widely studied in neutral carbohydrate chemistry,[18] where it has also been used to access thioglycopyranoside-containing *S*-linked disaccharides,[20] but only recently has it received attention the sialic acid glycal series.[19]

In their pioneering studies on the Ferrier reaction of thiols with neutral hex-2-enopyranosides, A. Zamojski and W. Priebe,[21] and then other authors,[20,22,23] observed that, depending on the nature of the nucleophile and the reaction conditions, the rearrangement may result in the formation

Table 1. Ritter reaction conditions using CH_3CN as a reagent.[a]



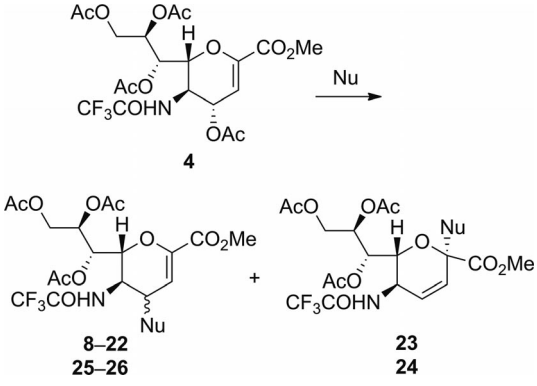
Entry	Lewis acid	Glycal [mmol]	Conditions *T* [°C] (*t* [h])	Solvent	Glycal **6** α/β ratio; yield [%]
1	$BF_3{\cdot}Et_2O$	10	40 (1)	CH_2Cl_2	2:3; 81
2	$BF_3{\cdot}Et_2O$	10	40 (1)	CH_3NO_2	2:3; 81
3	$BF_3{\cdot}Et_2O$	1	40 (48)	CH_2Cl_2	2:3; 75
4	$BF_3{\cdot}Et_2O$	10	25 (48)	CH_2Cl_2	2:3; 52
5	$BF_3{\cdot}Et_2O$	1	40 (48)	CH_3NO_2	2:3; 68
6	$BF_3{\cdot}Et_2O$	10	25 (48)	CH_3NO_2	2:3; 70
7	TMSOTf	10	40 (1)	CH_2Cl_2	2:3; 79
8	TMSOTf	1	40 (1)	CH_3NO_2	2:3; 65
9	TMSOTf	10	25 (48)	CH_2Cl_2	2:3; 64
10	H_2SO_4	10	50 (48)	THF	2:3; 27
11	H_2SO_4	10	25 (48)	THF	2:3; 20

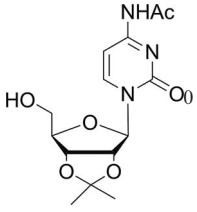
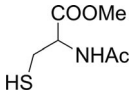
[a] Experimental conditions: glycal (0.2 mmol) in solvent (1.5 mL), CH_3CN (2 mmol).

of a thioglycoside alone, or together with a 3-thioglycal as a minor regioisomer. The former is the kinetic product of reaction, the latter the thermodynamic product. These authors isolated the rearranged isomer in increased amounts after prolonged treatment of the reaction mixture with the Lewis acid, or even after chromatography of the reaction mixture on silica.[24,25]

Thus, we considered that the different regiochemistry observed in the reaction with protected cysteine (Table 2, entry 18) and simpler thiols (Table 2, entries 15–17) could signify that, in sialic acid glycals, thiols first attack the anomeric carbon in a kinetically controlled reaction, and then undergo equilibration to thermodynamically more stable glycals with the nucleophile bound to the carbon bearing the leaving group. This is consistent with the well-known ability of sulfides to rearrange under Lewis or Brønsted acidic conditions.[20–23] The equilibration could be easier for simple thiols and more difficult for cysteine, probably as a

Table 2. Intermolecular nucleophilic attack on Neu5-perfluoroacetylated glycals.[a]

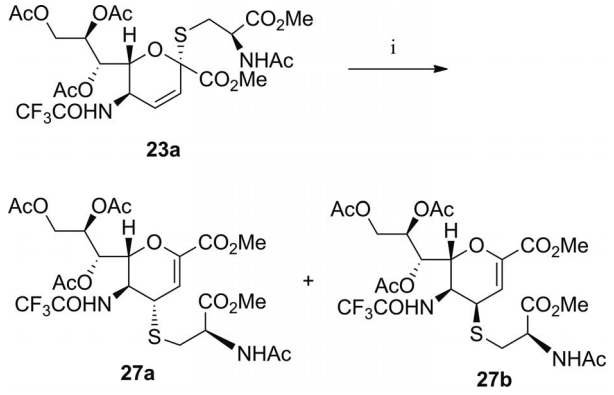


Entry	Nucleophile	*t* [min]	Products; a = α, b = β	α/β ratio; yield [%]
1	$MeSO_2NH_2$	15	**8b**	4β only; 87
2	$PhSO_2NH_2$	15	**9b**	4β only; 88
3	$pCH_3PhSO_2NH_2$	15	**10b**	4β only; 86
4	MeOH	15	**11b**	4β only; 81
5	EtOH	15	**12b**	4β only; 79
6	*n*PrOH	30	**13b**	4β only; 71
7	*n*BuOH	30	**14b**	4β only; 74
8	*i*PrOH	60	**15a + 15b**	1:2; 75
9	BnOH	60	**16b**	4β only; 83
10			**17b**	4β only; 58
11	*t*BuOH	60	–	0
12	phenol	120	–	0
13	4-chlorophenol	60	**18b**	4β only; 67
14	4-methylphenol	60	**19a**	4α only; 56
15	EtSH	15	**20a + 20b**	2:1; 85
16	$C_8H_{17}SH$	30	**21a**	4α only; 61
17	PhSH	15	**22a + 22b**	5:1; 84
18		60	**23a**	2α only; 79
19	TESH	15	**24a**	2α only; 86
20	TMSCl	15	**25a + 25b**	1:3; 78
21	TMSBr	30	**26b**	4β only; 73

[a] Experimental conditions: glycal (0.2 mmol) in solvent (1.5 mL), CH_3CN (2 mmol).

consequence of the amino acidic functionality, which may coordinate to the acetoxy leaving group, or which, in some way, may cause a major difference in energy between glycoside **23a** and its allylic regioisomer(s).[26]

In order to ascertain whether cysteine sialoside **23a**[27] could really be equilibrated to its 4α-substituted regioisomer, or to a mixture of 4α and 4β epimers, we heated it in dichloromethane containing an increased amount (20 equiv.) of $BF_3{\cdot}Et_2O$, for 2 h. After this treatment, sialoside **23a** gave 4-substituted glycals **27a** and **27b** (α/β ratio: 2:1; Scheme 2), which suggests that also the 4α-substituted thioglycals obtained with simple thiols (Table 2, entries 15–17) could derive from the equilibration of first-formed 2-substituted sialosides.

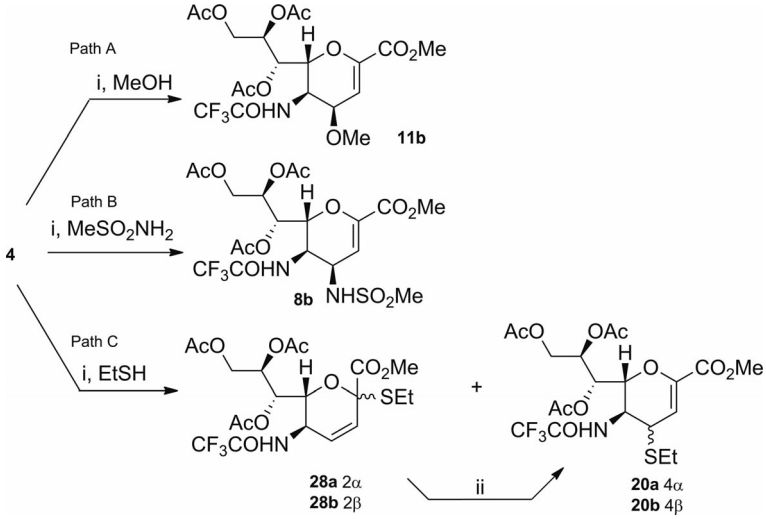


Scheme 2. Acidic rearrangement of cysteine Ferrier sialoside. *Reagents and conditions:* (i) $BF_3{\cdot}Et_2O$ (20 equiv.), CH_2Cl_2, 40 °C, 2 h.

This hypothesis could also explain their α stereochemistry at C-4, opposite to that observed with other nucleophiles that could arise from direct attack at C-4 from the most favoured β face of the molecule.[12]

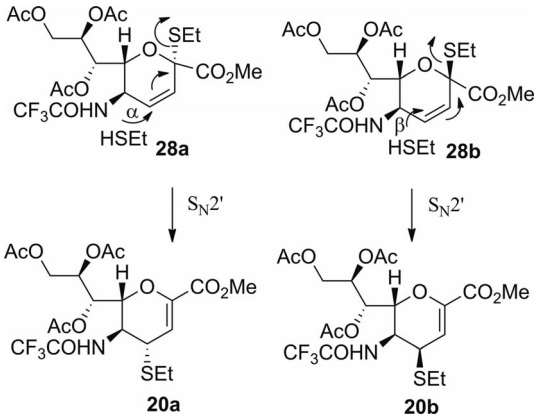
To ascertain this, we designed two experiments. The first aimed to trap the possible Ferrier glycosides formed in the reactions, the second to verify the ability of these possible first-formed sialosides to rearrange into their 4-substituted regioisomers. Thus, we first treated FANA glycal **4** with MeOH, $MeSO_2NH_2$, and EtSH (O, N, and S nucleophiles) under milder conditions (23 °C) in separate experiments, and monitored the course of the reactions by TLC and NMR spectroscopy. In this way, in the first two reactions, we observed only the presence of the 4β-substituted epimers (i.e., **11b** or **8b**, respectively; Scheme 3, Path A and Path B). They formed after a few minutes and increased until the end of the reaction, i.e., the complete consumption of stating glycal **4**.[28] In contrast, in the reaction of glycal **4** with EtSH, we initially observed the formation of the 2α and 2β isomeric sialosides (i.e., **28a** and **28b**),[27] together with the two 4α- and 4β-substituted analogues (i.e., **20a** and **20b**; as shown by ^1H NMR spectroscopy and TLC), all of which remained present until the complete disappearance of the starting glycal. After the reaction was complete, we isolated epimeric thioglycosides **28a** and **28b**, together with regioisomer **20b**, as an inseparable mixture, and also glycal **20a** as a pure compound. Both the pairs of diastereomers showed the prevalence of the α over the β epimer (2:1; see Experimental section). Moreover, after heating the reaction mixture at 40 °C for an additional time (15 min), we isolated only the diastereomeric pair of thioesters **20a** and **20b** (2:1 ratio) in 80% yield.

These results strongly suggest that the reaction of protected FANA glycal **4** with thiols could follow a different course from that of oxygen or nitrogen nucleophiles, since they first give Ferrier products that are subsequently isomerized to give a pair of glycalic 4-substituted thioethers **20a** and **20b**. Moreover, since thioethers **20a** and **20b** were isolated with the same α/β ratio as the parent sialosides (i.e.,



Scheme 3. Allylic substitution and internal *S*-rearrangement. *Reagents and conditions:* (i) $BF_3{\cdot}Et_2O$ (1 equiv.), CH_2Cl_2, 25 °C; (ii) $BF_3{\cdot}Et_2O$ (10 equiv.), CH_2Cl_2, 40 °C.

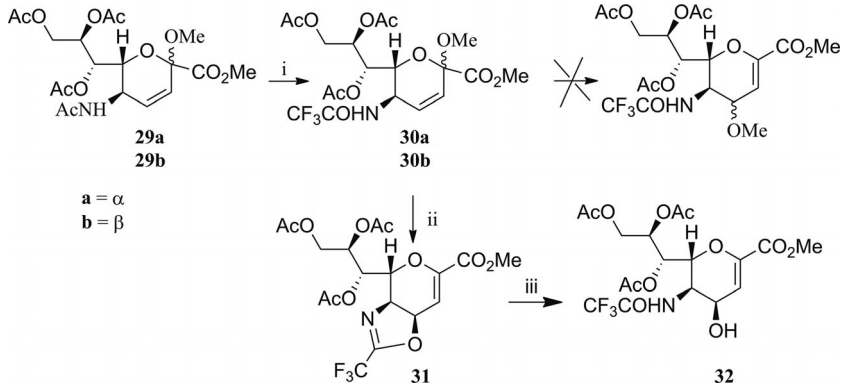
28a and **28b**), it appeared to be possible that a concerted mechanism of isomerization could be operating in the equilibration of simpler thiols, probably through two parallel S_N2' processes (Scheme 4).



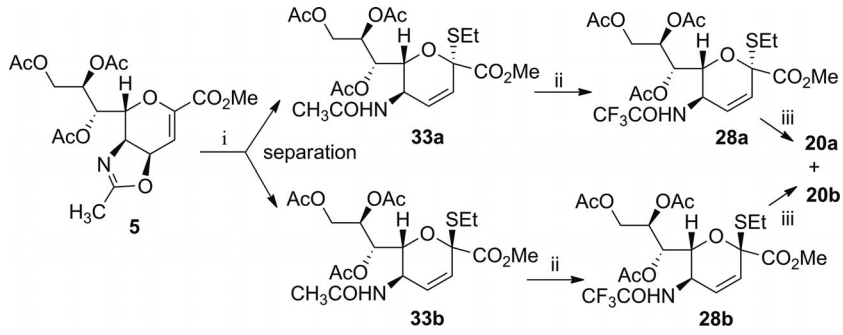
Scheme 4. Possible concerted equilibration of thiolic sialosides.

To support or exclude this idea, we *N*-transacylated Ferrier glycosides **29a** and **29b**[19] to give *O*-sialosides **30a** and **30b**, and subjected these compounds to acidic treatment with $BF_3{\cdot}Et_2O$ (10 equiv., for 15 min) in dichloromethane in separate experiments (Scheme 5). In neither of the reactions did we obtain any glycal deriving from isomerization of the acetalic groups; we observed only the formation of perfluorinated oxazoline **31**, which was isolated as such or as 4β-hydroxy FANA glycal **32**.[13] Clearly, the acidic treatment causes a simple elimination of the 2-methoxy groups, the rearrangement of which is probably hindered by the immediate formation of oxazoline **31**. This result strongly supports the possibility that, in our reaction, alcohols directly attack C-4 of FANA glycal **4**, attacking the molecule from the less hindered β-side (Table 2).[12]

In a parallel experiment, we prepared thioglycosides **28a** and **28b**,[27] in pure form, as single isomers, by an independent route, and tested their possible rearrangement into glycals **20a** and **20b** (Scheme 6). For their preparation, we first treated oxazoline **5** with ethanethiol in the presence of Bi(OTf)$_3$, and obtained unfluorinated thioglycosides **33a** and



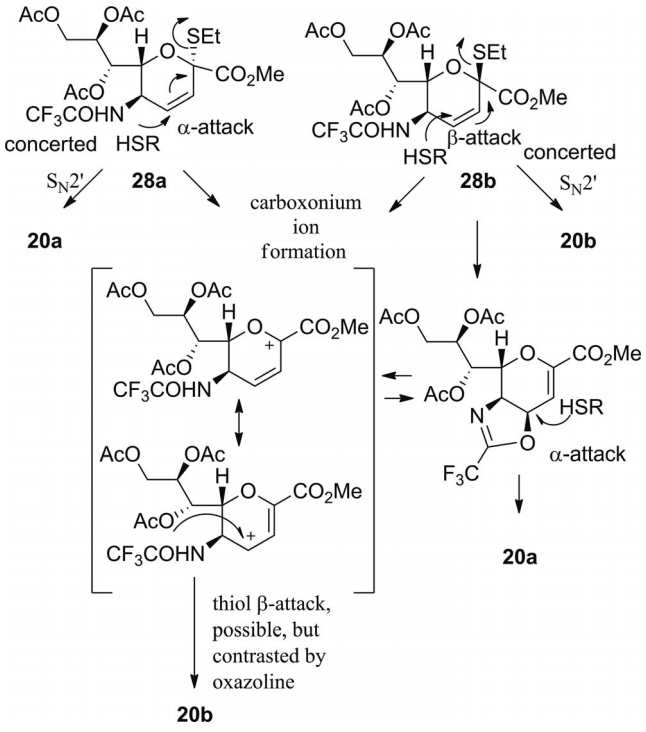
Scheme 5. Synthesis and acidic equilibration of Ferrier sialosides **30a** and **30b**. *Reagents and conditions:* (i) $(CF_3CO)_2O$, Et_3N, CH_3CN, 135 °C, 5 min; (ii) CH_3OH (10 equiv.), $BF_3{\cdot}Et_2O$ (10 equiv.), CH_2Cl_2, 40 °C, 15 min, then Et_3N (0.1 mL), CH_2Cl_2, H_2O; (iii) CH_3OH (10 equiv.), $BF_3{\cdot}Et_2O$ (10 equiv.), CH_2Cl_2, 40 °C, 15 min, then H_2O, CH_2Cl_2.



Scheme 6. Synthesis and acidic equilibration of diastereomerically pure Ferrier thiosialosides **28a** and **28b**. (ii) $(CF_3CO)_2O$, Et_3N, CH_3CN, 135 °C, 5 min; (iii) EtSH (10 equiv.), $BF_3{\cdot}Et_2O$ (10 equiv.), CH_2Cl_2, 40 °C, 15 min.

33b,[27] which could be separated by rapid chromatography and transformed, by direct *N*-transacylation, into the corresponding perfluorinated thioglycosides (i.e., **28a** and **28b**; Scheme 6). Each of them was completely characterized and then subjected to separate treatment with EtSH and $BF_3{\cdot}Et_2O$ in dichloromethane, for 15 min at 40 °C, a process that transformed them into two very similar mixtures of the 4α- and 4β-thioether derivatives (i.e., **20a** and **20b**), which were obtained in comparably high yields and with very close epimeric ratios (α/β: 2.3:1.0).

These results confirm that the 4-substituted glycals formed in the reactions with thiols, can derive from isomerization of first-formed thioglycosides.[28] Moreover, they also show that the isomerization reactions of the simple thiol derivatives follow a course similar to that of sialosyl cysteine **23a**. A single mechanism has not been identified for this process, but it may involve, in combination, a series of alternative pathways, which we have summarized in Scheme 7. The possibility of an equilibration of the 4α- and 4β-substituted epimers (i.e., **20a** and **20b**) was excluded by an experiment involving the separate acidic treatment of these two thioethers ($BF_3{\cdot}Et_2O$ for 15 min at 40 °C). In the Scheme, we hypothesized that, under our reaction conditions, different routes can contribute to the final result. We considered a concerted mechanism, and the intermediate formation of a discrete carboxonium ion and/or of a possible transient perfluorinated oxazoline. However, in absence of other evidence, we cannot decide which is the major contributing mechanism.



Scheme 7. Possible contributing events resulting in the formation of 4-substituted thioglycals **20a** and **20b**.

Conclusions

In conclusion, we have developed a general protocol for the synthesis of 4-substituted 2,3-unsaturated neuraminic acid derivatives (FANA and DANA glycals) containing elements of molecules with anti-NA activity. The protocol involves the reaction of a protected FANA glycal with various nucleophiles in the presence of a Lewis acid. Under our reaction conditions, direct allylic substitution at C-4 occurs with oxygen or nitrogen nucleophiles, while with thiols, the reaction goes through a Ferrier reaction and a subsequent equilibration. Thus, our results expand the applicability of Ferrier reaction to C-4-functionalized sialic acid glycals, highlighting its synthetic utility for the preparation of these highly sought after compounds.

Experimental Section

General Remarks: Nuclear magnetic resonance spectra were recorded at 298 K operating at 500.13 MHz for ^1H and 125.76 MHz for ^{13}C. Chemical shifts are reported in parts per million (ppm, δ units). In $CDCl_3$, chemical shifts were calibrated to the residual $CDCl_3$ signal (δ = 7.26 ppm for ^1H and at δ = 77.0 ppm for ^{13}C spectra). In D_2O spectra, chemical shifts were calibrated to *t*BuOH as an internal standard (δ = 1.24 ppm for ^1H and at δ = 30.29 ppm for ^{13}C spectra). Proton and carbon assignments were established, if necessary, using ^1H–^1H and ^1H–^{13}C correlated NMR experiments. ^1H NMR spectroscopic data are tabulated in the following order: multiplicity (s, singlet; d, doublet; t, triplet; br. s, broad singlet; m, multiplet), coupling constant(s) in Hertz, number of pro-

tons, assignment of proton(s). Optical rotations were recorded using a polarimeter equipped with a 1 dm cell. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}, and the concentrations are given in g 100 mL^{-1}. Mass spectrometry was performed using a quadrupole ion trap mass spectrometer equipped with an electrospray (ESI) ion source. The spectra were collected in continuous flow mode by connecting the infusion pump directly to the ESI source. Solutions of compounds were infused at a flow rate of 5 μL min^{-1}. The spray voltage was set at 5.0 kV in the positive and at 4.5 kV in the negative ion mode, with a capillary temperature of 220 °C. Full-scan mass spectra were recorded by scanning a *m*/*z* range of 100–2000. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F 254), visualized using UV light, 50% sulfuric acid, or 0.2% ninhydrin in ethanol and heat. Usual work-up, unless otherwise indicated, refers to the following sequence: Et_3N (0.1 mL) was added to the reaction mixtures, the solvents were evaporated under a nitrogen flow and reduced pressure, the residue was diluted with EtOAc, and the organic phase was washed with ice-cold $NaHCO_3$ (saturated aq.). Finally, the organic phase was dried with Na_2SO_4 and filtered, and the solvents were evaporated.

Ritter Reaction Using CH_3CN as a Reagent, with Different Solvents and Lewis Acids

Methyl 7,8,9-Tri-*O*-acetyl-4-(acetylamino)-2,6-anhydro-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (6a) and Methyl 7,8,9-Tri-*O*-acetyl-4-(acetylamino)-2,6-anhydro-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (6b): Glycal **4** was dissolved in the appropriate solvent (1.5 mL) and treated with CH_3CN (2.0 mmol). The parameters that were modified (i.e., temperature, time, and catalyst, as well as the yields) are reported in Table 1. The reaction mixtures were worked up as indicated in the General Remarks to give, after flash chromatography, eluting with EtOAc/hexane (80:20 v/v), the less polar glycal (i.e., **6b**), followed by the more polar glycal (i.e., **6a**), both in pure form.

Data for Glycal 6b: M.p. 133–135 °C (CH_2Cl_2/diisopropyl ether). $C_{20}H_{25}F_3N_2O_{11}$ (526.41): calcd. C 45.63, H 4.79, N 5.32; found C 45.56, H 4.67, N 5.30.

Data for Glycal 6a: M.p. 146–148 °C (CH_2Cl_2/diisopropyl ether). $C_{20}H_{25}F_3N_2O_{11}$ (526.41): calcd. C 45.63, H 4.79, N 5.32; found C 45.56, H 4.67, N 5.30. All other physico-chemical properties were practically identical to those previously reported.

Reaction of Perfluorinated Glycal 4 with Different Nucleophiles under BF_3·Et_2O Catalysis: The reactions were performed on starting glycal **4** (0.2 mmol) dissolved in CH_2Cl_2 (1.5 mL), using the appropriate nucleophile (2.0 mmol) and BF_3·Et_2O (246 μL, 2.0 mmol) at 40 °C for the time indicated in Table 2. Then, the reaction mixtures were worked-up as indicated in the General Remarks to give, after flash chromatography, the appropriate glycal.

In some cases, the reactions were additionally performed on glycal **4** (0.2 mmol) dissolved in CH_2Cl_2 (1.5 mL), with the appropriate nucleophile (2.0 mmol) and BF_3·Et_2O (25 μL, 0.2 mmol) at 25 °C.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,4,5-trideoxy-4-[(methylsulfonyl)amino]-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (8b)

Method 1: Glycal **8b** (98 mg, 87%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with $MeSO_2NH_2$ (190 mg), heating for 15 min at 40 °C in CH_2Cl_2, m.p. 155–157 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –72.8 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.63 (d, $J_{NH,5}$ = 10.0 Hz, 1 H, N-H), 6.09 (d, $J_{3,4}$ = 5.7 Hz, 1 H, 3-H), 5.58 (d, $J_{NH,4}$ = 9.0 Hz, 1 H, H-NSO_2), 5.48 (dd, $J_{7,6}$ = 2.2, $J_{7,8}$ = 4.1 Hz, 1 H, 7-H), 5.36 (ddd, $J_{8,9a}$ = 2.7, $J_{8,7}$ = 4.1, $J_{8,9b}$ = 7.9 Hz, 1 H, 8-H), 4.78 (dd, $J_{9a,8}$ = 2.7, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.40 (ddd, $J_{5,4}$ = 4.7, $J_{5,6}$ = $J_{5,NH}$ = 10.0 Hz, 1 H, 5-H), 4.28 (dd, $J_{6,7}$ = 2.2, $J_{6,5}$ = 10.0 Hz, 1 H, 6-H), 4.19–4.10 (overlapping, 2 H, 9b-H and 4-H), 3.81 (s, 3 H, $COOCH_3$), 3.03 (s, 3 H, $NHSO_2CH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.08 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ =171.0, 170.9 (2 C, O*C*OCH$_3$ at C-8 and O*C*OCH$_3$ at C-9), 169.8 (O*C*OCH$_3$ at C-7), 161.6 (C-1), 157.6 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 145.5 (C-2), 119.0–110.0 (CF_3), 106.7 (C-3), 72.9 (C-6), 71.4 (C-8), 67.9 (C-7), 62.2 (C-9), 52.8 ($COOCH_3$), 47.1 (C-4), 46.3 (C-5), 41.2 (SO_2CH_3), 20.9, 20.7, 20.4 (3C, OCO*C*H$_3$) ppm. MS (ESI$^+$): *m*/*z* = 563.7 [M + H]$^+$, 585.5 [M + Na]$^+$, 1150.1 [2M + Na]$^+$. $C_{19}H_{25}F_3N_2O_{12}S$ (562.47): calcd. C 40.57, H 4.48, N 4.98; found C 40.81, H 4.57, N 5.11.

Method 2: Glycal **8b** was also obtained by treating glycal **4** (105 mg, 0.2 mmol) in CH_2Cl_2 (1.5 mL) with $MeSO_2NH_2$ (190 mg, 2.0 mmol) and BF_3·Et_2O (25 μL, 0.2 mmol) at 25 °C for 48 h. Glycal **8b** (62 mg, 55%) was obtained as a white solid together with starting glycal **4** (32 mg, 30%).

Data for 8b: MS (ESI$^+$): *m*/*z* = 563.5 [M + H]$^+$, 585.2 [M + Na]$^+$. $C_{19}H_{25}F_3N_2O_{12}S$ (562.47): calcd. C 40.57, H 4.48, N 4.98; found C 40.68, H 4.51, N 5.01. All other physico-chemical properties were practically identical to those previously reported.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,4,5-trideoxy-4-[(phenylsulfonyl)amino]-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (9b): Glycal **9b** (110 mg, 88%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with $PhSO_2NH_2$ (314 mg), heating for 15 min at 40 °C in CH_2Cl_2, m.p. 127–129 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –15.7 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.88–7.83 (overlapping, 2 H, SO_2Ph), 7.75 (d, $J_{NH,5}$ = 9.2 Hz, 1 H, N-H), 7.64–7.57 (m, 1 H, SO_2Ph), 7.55–7.45 (overlapping, 2 H, SO_2Ph), 6.01 (d, $J_{NH,4}$ = 8.5 Hz, 1 H, H-NSO_2), 5.52 (d, $J_{3,4}$ = 5.8 Hz, 1 H, 3-H), 5.49 (dd, $J_{7,6}$ = 1.8, $J_{7,8}$ = 5.0 Hz, 1 H, 7-H), 5.39 (ddd, $J_{8,9a}$ = 2.7, $J_{8,7}$ = 5.0, $J_{8,9b}$ = 7.4 Hz, 1 H, 8-H), 4.66 (dd, $J_{9a,8}$ = 2.7, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.36–4.29 (m, 1 H, 5-H), 4.28 (dd, $J_{6,7}$ = 1.8, $J_{6,5}$ = 10.8 Hz, 1 H, 6-H), 4.14 (dd, $J_{9b,8}$ = 7.4, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.80–3.85 (m, 1 H, 4-H), 3.71 (s, 3 H, $COOCH_3$), 2.09 (s, 3 H, O*C*OCH$_3$), 2.08 (s, 3 H, O*C*OCH$_3$), 2.04 (s, 3 H, O*C*OCH$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.9, 169.7 (3 C, O*C*OCH$_3$), 161.6 (C-1), 157.6 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 145.4 (C-2), 139.5, 133.4, 129.5, 126.9 (6 C, Ph), 119.0–110.0 (CF_3), 106.1 (C-3), 72.7 (C-6), 70.8 (C-8), 67.8 (C-7), 62.3 (C-9), 52.6 (COO*C*H$_3$), 46.9 (C-4), 46.2 (C-5), 20.7, 20.6, 20.4 (3 C, O*C*OCH$_3$) ppm. MS (ESI$^+$): *m*/*z* = 625.2 [M + H]$^+$, 647.3 [M + Na]$^+$, 1271.4 [2M + Na]$^+$. $C_{24}H_{27}F_3N_2O_{12}S$ (624.54): calcd. C 46.16, H 4.36, N 4.49; found C 45.97, H 4.21, N 4.33.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,4,5-trideoxy-4-{[(4-methylphenyl)sulfonyl]amino}-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (10b): Glycal **10b** (110 mg, 86%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with *p*-toluenesulfonamide (342 mg), heating for 15 min at 40 °C in CH_2Cl_2, m.p. 133–135 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –21.3 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.74–7.69 (overlapping, 2 H, SO_2PhCH_3), 7.49 (d, $J_{NH,5}$ = 9.3 Hz, 1 H, N-H), 7.25–7.30 (overlapping, 2 H, SO_2PhCH_3), 5.61 (d, $J_{NH,4}$ = 8.0 Hz, 1 H, H-NSO_2), 5.54 (d, $J_{3,4}$ = 5.8 Hz, 1 H, 3-H), 5.48 (dd, $J_{7,6}$ = 2.0, $J_{7,8}$ = 5.1 Hz, 1 H, 7-H), 5.40 (ddd, $J_{8,9a}$ = 2.7, $J_{8,7}$ = 5.1, $J_{8,9b}$ = 7.4 Hz, 1 H, 8-H), 4.65 (dd, $J_{9a,8}$ = 2.7, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.36–4.30 (m, 1 H, 5-H), 4.23 (dd, $J_{6,7}$ = 2.0, $J_{6,5}$ = 10.9 Hz, 1 H, 6-H), 4.13 (dd, $J_{9b,8}$ = 7.4, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.84 (ddd, $J_{4,5}$

= 4.6, $J_{4,3}$ = 5.8, $J_{4,NH}$ = 8.0 Hz, 1 H, 4-H), 3.74 (s, 3 H, $COOCH_3$), 2.44 (s, 3 H, SO_2PhCH_3), 2.08 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.03 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.9, 170.8, 169.7 (3 C, $OCOCH_3$), 161.6 (C-1), 157.7 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.6 (C-2), 144.6, 135.2, 130.1, 127.1 (6 C, Ph), 119.0–110.0 (CF_3), 106.0 (C-3), 72.8 (C-6), 70.8 (C-8), 67.7 (C-7), 62.2 (C-9), 52.6 ($COOCH_3$), 47.0 (C-4), 46.1 (C-5), 21.6 ($PhCH_3$), 20.8, 20.6, 20.4 (3 C, $OCOCH_3$) ppm. MS (ESI^+): *m*/*z* = 639.4 [M + H]$^+$, 661.3 [M + Na]$^+$, 1300.0 [2M + Na]$^+$. $C_{25}H_{29}F_3N_2O_{12}S$ (638.56): calcd. C 47.02, H 4.58, N 4.39; found C 47.21, H 4.57, N 4.31.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-methyl-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (11b)

Method 1: Glycal **11b** (81 mg, 81%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with MeOH (81 μL), heating for 15 min at 40 °C in CH_2Cl_2, m.p. 122–124 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –11.3 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.71 (d, $J_{NH,5}$ = 9.5 Hz, 1 H, N-H), 6.26 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.39 (dd, $J_{7,6}$ = 2.1, $J_{7,8}$ = 5.0 Hz, 1 H, 7-H), 5.33 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 5.0, $J_{8,9b}$ = 6.9 Hz, 1 H, 8-H), 4.66 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.41–4.36 (m, 1 H, 5-H), 4.33 (dd, $J_{6,7}$ = 2.1, $J_{6,5}$ = 10.7 Hz, 1 H, 6-H), 4.14 (dd, $J_{9b,8}$ = 6.9, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.82 (s, 3 H, $COOCH_3$), 3.80 (dd, $J_{4,5}$ = 3.9, $J_{4,3}$ = 5.3 Hz, 1 H, 4-H), 3.44 (s, 3 H, OCH_3), 2.10 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1, 169.7 (3 C, $OCOCH_3$), 161.7 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.9 (C-2), 119.0–110.0 (CF_3), 105.9 (C-3), 73.1 (C-6), 71.0 (C-8), 69.2 (C-4), 67.6 (C-7), 62.1 (C-9), 56.6 (OCH_3), 52.6 ($COOCH_3$), 46.2 (C-5), 20.9, 20.7, 20.6 (3 C, $OCOCH_3$) ppm. MS (ESI^+): *m*/*z* = 500.6 [M + H]$^+$, 523.5 [M + Na]$^+$. $C_{19}H_{24}F_3NO_{11}$ (499.39): calcd. C 45.70, H 4.84, N 2.80; found C 45.88, H 5.02, N 2.88.

Method 2: Glycal **11b** was also obtained by treating glycal **4** (105 mg, 0.2 mmol) in CH_2Cl_2 (1.5 mL) with MeOH (81 μL, 2.0 mmol) and $BF_3{\cdot}Et_2O$ (25 μL, 0.2 mmol), at 25 °C for 48 h. Glycal **11b** (45 mg, 45%) was obtained as a white solid together with starting glycal **4** (37 mg, 35%).

Data for 11b: MS (ESI^+): *m*/*z* = 500.1 [M + H]$^+$, 523.7 [M + Na]$^+$. $C_{19}H_{24}F_3NO_{11}$ (499.39): calcd. C 45.70, H 4.84, N 2.80; found C 45.93, H 5.00, N 2.79. All other physico-chemical properties were practically identical to those previously reported.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-ethyl-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (12b): Glycal **12b** (81 mg, 79%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with EtOH (117 μL), heating for 15 min at 40 °C in CH_2Cl_2, m.p. 135–137 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –55.3 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.71 (d, $J_{NH,5}$ = 9.3 Hz, 1 H, N-H), 6.24 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.41 (dd, $J_{7,6}$ = 2.1, $J_{7,8}$ = 4.9 Hz, 1 H, 7-H), 5.33 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 4.9, $J_{8,9b}$ = 7.1 Hz, 1 H, 8-H), 4.69 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.40–4.35 (m, 1 H, 5-H), 4.33 (dd, $J_{6,7}$ = 2.1, $J_{6,5}$ = 10.6 Hz, 1 H, 6-H), 4.15 (dd, $J_{9b,8}$ = 7.1, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.89 (dd, $J_{4,5}$ = 4.0, $J_{4,3}$ = 5.3 Hz, 1 H, 4-H), 3.82 (s, 3 H, $COOCH_3$), 3.78–3.73 (m, 1 H, OCH_2CH_3), 3.53–3.46 (m, 1 H, OCH_2CH_3), 2.11 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$), 1.24–1.20 (m, 3 H, OCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.2, 169.7 (3 C, $OCOCH_3$), 161.8 (C-1), 157.1 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.6 (C-2), 119.0–110.0 (CF_3), 106.8 (C-3), 73.1 (C-6), 71.1 (C-8), 67.7 (C-4), 67.6 (C-7), 64.8 (OCH_2CH_3), 62.1 (C-9), 52.6 ($COOCH_3$), 46.2 (C-5), 20.9, 20.7, 20.6 (3 C, $OCOCH_3$), 15.3 (OCH_2CH_3) ppm. MS (ESI^+): *m*/*z* = 514.5 [M + H]$^+$, 536.4 [M + Na]$^+$. $C_{20}H_{26}F_3NO_{11}$ (513.42): calcd. C 46.79, H 5.10, N 2.73; found C 46.51, H 5.01, N 2.50.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-propyl-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (13b): Glycal **13b** (75 mg, 71%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with *n*PrOH (150 μL), heating for 30 min at 40 °C in CH_2Cl_2, m.p. 124–127 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –38.2 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.71 (d, $J_{NH,5}$ = 9.5 Hz, 1 H, N-H), 6.24 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.41 (dd, $J_{7,6}$ = 2.2, $J_{7,8}$ = 5.0 Hz, 1 H, 7-H), 5.35 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 5.0, $J_{8,9b}$ = 6.9 Hz, 1 H, 8-H), 4.68 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.40–4.35 (m, 1 H, 5-H), 4.32 (dd, $J_{6,7}$ = 2.2, $J_{6,5}$ = 10.6 Hz, 1 H, 6-H), 4.15 (dd, $J_{9b,8}$ = 6.9, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.88 (dd, $J_{4,5}$ = 4.0, $J_{4,3}$ = 5.3 Hz, 1 H, 4-H), 3.81 (s, 3 H, $COOCH_3$), 3.69–3.63 (m, 1 H, $OCH_{2a}CH_2CH_3$), 3.41–3.34 (m, 1 H, $OCH_{2b}CH_2CH_3$), 2.10 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$), 1.67–1.54 (overlapping, 2 H, $OCH_2CH_2CH_3$), 0.92 (m, 3 H, $OCH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1, 169.7 (3 C, $OCOCH_3$), 161.8 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.6 (C-2), 119.0–110.0 (CF_3), 106.8 (C-3), 73.1 (C-6), 71.0 (C-8), 70.9 (OCH_2CH_2), 67.8 (C-7), 67.6 (C-4), 62.1 (C-9), 52.6 ($COOCH_3$), 46.3 (C-5), 22.9 ($OCH_2CH_2CH_3$), 20.9, 20.7, 20.6 (3 C, $OCOCH_3$), 10.4 ($OCH_2CH_2CH_3$) ppm. MS (ESI^+): *m*/*z* = 528.4 [M + H]$^+$, 551.4 [M + Na]$^+$. $C_{21}H_{28}F_3NO_{11}$ (527.44): calcd. C 47.82, H 5.35, N 2.66; found C 47.69, H 5.40, N 2.62.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-4-*O*-butyl-3,5-dideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (14b): Glycal **14b** was obtained as a white solid (80 mg, 74%) by the reaction of glycal **4** (105 mg, 0.2 mmol) with *n*BuOH (183 μL), heating for 30 min at 40 °C in CH_2Cl_2, m.p. 118–121 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –36.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.72 (d, $J_{NH,5}$ = 9.5 Hz, 1 H, N-H), 6.24 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.41 (dd, $J_{7,6}$ = 2.2, $J_{7,8}$ = 4.9 Hz, 1 H, 7-H), 5.34 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 4.9, $J_{8,9b}$ = 7.0 Hz, 1 H, 8-H), 4.69 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.40–4.34 (m, 5-H), 4.32 (dd, $J_{6,7}$ = 2.2, $J_{6,5}$ = 10.6 Hz, 1 H, 6-H), 4.16 (dd, $J_{9b,8}$ = 7.0, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.87 (dd, $J_{4,5}$ = 4.0, $J_{4,3}$ = 5.3 Hz, 1 H, 4-H), 3.82 (s, 3 H, $COOCH_3$), 3.73–3.67 [m, 1 H, $OCH_{2a}(CH_2)_2CH_3$], 3.45–3.38 [m, 1 H, $OCH_{2b}(CH_2)_2CH_3$], 2.11 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$), 1.60–1.52 (overlapping, 2 H, $OCH_2CH_2CH_2CH_3$), 1.42–1.31 [overlapping, 2 H, $O(CH_2)_2CH_2CH_3$], 0.93 (m, 3 H, $OCH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.2, 169.7 (3 C, $OCOCH_3$), 161.8 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.6 (C-2), 119.0–110.0 (CF_3), 106.8 (C-3), 73.2 (C-6), 71.1 (C-8), 69.1 [$OCH_2(CH_2)_2CH_3$], 67.8 (C-7), 67.6 (C-4), 62.1 (C-9), 52.6 ($COOCH_3$), 46.3 (C-5), 31.7 ($OCH_2CH_2CH_2CH_3$), 20.9, 20.7, 20.6 (3 C, $OCOCH_3$), 19.2 [$O(CH_2)_2CH_2CH_3$], 13.7 [$O(CH_2)_3CH_3$] ppm. MS (ESI^+): *m*/*z* = 542.4 [M + H]$^+$, 564.5 [M + Na]$^+$. $C_{22}H_{30}F_3NO_{11}$ (541.47): calcd. C 48.80, H 5.58, N 2.59; found C 48.98, H 5.48, N 2.43.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-isopropyl-5-[(trifluoroacetyl)amino]-D-glycero-D-galacto-non-2-enonate (15a) and Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-isopropyl-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (15b): Starting from glycal **4** (105 mg, 0.2 mmol) and *i*PrOH (153 μL), after heating for 60 min at 40 °C in CH_2Cl_2, a mixture of glycals **15b** and **15a** was obtained. This mixture was separated by rapid chromatography, eluting with hexane/EtOAc (80:20 v/v), to give less polar glycal **15b** (53 mg, 50%), followed by more polar glycal **15a** (26 mg, 25%), both in pure form.

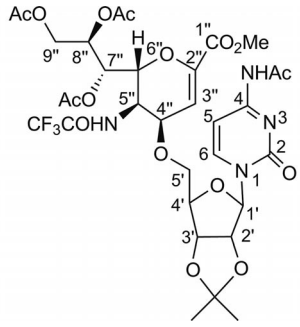
Data for Glycal 15a: M.p. 136–138 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = +33.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.65 (d,

$J_{NH,5}$ = 8.0 Hz, 1 H, N-H), 6.10 (d, $J_{3,4}$ = 3.3 Hz, 1 H, 3-H), 5.48 (dd, $J_{7,6}$ = $J_{7,8}$ = 4.7 Hz, 1 H, 7-H), 5.39 (ddd, $J_{8,9a}$ = 3.9, $J_{8,7}$ = 4.7, $J_{8,9b}$ = 5.6 Hz, 1 H, 8-H), 4.56 (dd, $J_{6,7}$ = 4.7, $J_{6,5}$ = 7.7 Hz, 1 H, 6-H), 4.49 (dd, $J_{9a,8}$ = 3.9, $J_{9a,9b}$ = 12.2 Hz, 1 H, 9a-H), 4.33 (dd, $J_{4,3}$ = 3.3, $J_{4,5}$ = 6.3 Hz, 1 H, 4-H), 4.20 (dd, $J_{9b,8}$ = 5.6, $J_{9b,9a}$ = 12.2 Hz, 1 H, 9b-H), 4.00–3.93 (m, 1 H, 5-H), 3.84–3.77 [overlapping, 4 H, $COOCH_3$ and $OCH(CH_3)_2$], 2.12 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.03 (s, 3 H, $OCOCH_3$), 1.18 [d, $J_{CH,(CH3)2a}$ = 6.1 Hz, 3 H, $OCH(CH_3)_{2a}$], 1.15 [d, $J_{CH,(CH3)2b}$ = 6.1 Hz, 3 H, $OCH(CH_3)_{2b}$] ppm. ^{13}C NMR ($CDCl_3$): δ = 170.5, 170.2, 169.7 (3 C, $OCOCH_3$), 161.8 (C-1), 157.1 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 143.2 (C-2), 119.0–105.5 (CF_3), 109.8 (C-3), 74.5 (C-6), 71.7 [$OCH(CH_3)_2$], 69.7 (C-8), 68.8 (C-4), 67.9 (C-7), 61.6 (C-9), 52.5 ($COOCH_3$), 50.1 (C-5), 22.9 [$OCH(CH_3)_{2a}$], 21.7 [$OCH(CH_3)_{2b}$], 20.8, 20.7, 20.5 (3 C, $OCOCH_3$) ppm. MS (ESI$^+$): *m*/*z* = 528.3 [M + H]$^+$, 551.4 [M + Na]$^+$. $C_{21}H_{28}F_3NO_{11}$ (527.44): calcd. C 47.82, H 5.35, N 2.66; found C 47.62, H 5.48, N 2.53.

Data for 15b: M.p. 141–143 °C. $[\alpha]_D$ = 24.2 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 6.70 (d, $J_{NH,5}$ = 9.4 Hz, 1 H, N-H), 6.17 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.41 (dd, $J_{7,6}$ = 2.2, $J_{7,8}$ = 4.8 Hz, 1 H, 7-H), 5.34 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 4.8, $J_{8,9b}$ = 7.1 Hz, 1 H, 8-H), 4.70 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.37–4.31 (m, 1 H, 5-H), 4.29 (dd, $J_{6,7}$ = 2.2, $J_{6,5}$ = 10.6 Hz, 1 H, 6-H), 4.16 (dd, $J_{9b,8}$ = 7.1, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.95 (dd, $J_{4,5}$ = 4.0, $J_{4,3}$ = 5.3 Hz, 1 H, 4-H), 3.84–3.75 [overlapping, 4 H, $COOCH_3$ and $OCH(CH_3)_2$], 2.10 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$), 1.20 [d, $J_{CH,(CH3)2a}$ = 6.1 Hz, 3 H, $OCH(CH_3)_{2a}$], 1.16 [d, $J_{CH,(CH3)2b}$ = 6.1 Hz, 3 H, $OCH(CH_3)_{2b}$] ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.2, 169.7 (3 C, $OCOCH_3$), 161.9 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.3 (C-2), 119.0–105.5 (CF_3), 107.8 (C-3), 73.1 (C-6), 71.4 [$OCH(CH_3)_2$], 71.2 (C-8), 67.6 (C-7), 65.8 (C-4), 62.1 (C-9), 52.6 ($COOCH_3$), 46.3 (C-5), 23.3 [$OCH(CH_3)_{2a}$], 21.7 [$OCH(CH_3)_{2b}$], 20.9, 20.7, 20.6 (3 C, $OCOCH_3$) ppm. MS (ESI$^+$): *m*/*z* = 528.3 [M + H]$^+$, 551.4 [M + Na]$^+$. $C_{21}H_{28}F_3NO_{11}$ (527.44): calcd. C 47.82, H 5.35, N 2.66; found C 47.62, H 5.48, N 2.49.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-4-*O*-benzyl-3,5-dideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (16b): Glycal **16b** (96 mg, 83%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with BnOH (207 μL), heating for 60 min at 40 °C in CH_2Cl_2, m.p. 119–121 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –31.1 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.43–7.27 (overlapping, 5 H, Ph), 6.75 (d, $J_{NH,5}$ = 8.0 Hz, 1 H, N-H), 6.28 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.42 (dd, $J_{7,6}$ = 1.4, $J_{7,8}$ = 5.2 Hz, 1 H, 7-H), 5.37 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 5.2, $J_{8,9b}$ = 6.8 Hz, 1 H, 8-H), 4.76 (d, $J_{CH2a,CH2b}$ = 11.4 Hz, 1 H, $OCH_{2a}Ph$), 4.70 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.5 Hz, 1 H, 9a-H), 4.49 (d, $J_{CH2b,CH2a}$ = 11.4 Hz, 1 H, $OCH_{2b}Ph$), 4.42–4.38 (overlapping, 2 H, 5-H and 6-H), 4.17 (dd, $J_{9b,8}$ = 6.8, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 4.00–3.98 (m, 1 H, 4-H), 3.85 (s, 3 H, $COOCH_3$), 2.12 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1, 169.7 (3 C, $OCOCH_3$), 161.8 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.9 (C-2), 136.6, 128.8, 128.6, 128.2 (6 C, Ph), 119.0–110.0 (CF_3), 106.2 (C-3), 73.1 (C-6), 71.1 (OCH_2Ph), 70.9 (C-8), 67.5 (C-7), 66.9 (C-4), 62.1 (C-9), 52.6 ($COOCH_3$), 46.2 (C-5), 20.9, 20.7, 20.6 (3 C, $OCOCH_3$) ppm. MS (ESI$^+$): *m*/*z* = 576.4 [M + H]$^+$, 598.5 [M + Na]$^+$. $C_{25}H_{28}F_3NO_{11}$ (575.49): calcd. C 52.18, H 4.90, N 2.43; found C 52.07, H 5.00, N 2.32.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-[*N*-acetyl-2′,3′-*O*-(1-methylethylidene)-cytidinyl]-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (17b):



Glycal **17b** (92 mg, 58%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with protected cytidine (130 mg, 0.4 mmol), heating for 120 min at 40 °C in CH_2Cl_2, m.p. 129–131 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –63.1 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 9.67 (br. s, 1 H, N*H*Ac), 9.29 (br. s, 1 H, N*H*$COCF_3$), 7.52 (d, $J_{6,5}$ = 7.4 Hz, 1 H, 6-H), 7.46 (d, $J_{5,6}$ = 7.4 Hz, 1 H, 5-H), 6.19 (d, $J_{3'',4''}$ = 5.3 Hz, 1 H, 3′′-H), 5.67–5.61 (overlapping, 2 H, 7′′-H and 8′′-H), 5.54 (d, $J_{2',3'}$ = 6.3 Hz, 1 H, 2′-H), 5.36 (s, 1 H, 1′-H), 5.20–5.15 (m, 1 H, 3′-H), 5.11 (dd, $J_{9a'',8''}$ = 1.6, $J_{9a'',9b''}$ = 12.1 Hz, 1 H, 9a′′-H), 4.43–4.31 (overlapping, 2 H, 5′′-H and 6′′-H), 4.20–4.14 (overlapping, 2 H, 4′-H and 9b′′-H), 4.01 (dd, $J_{5a',4'}$ = 1.8, $J_{5a',5b'}$ = 10.3 Hz, 1 H, 5a′-H), 3.86 (dd, $J_{4'',5''}$ = 3.8, $J_{4'',3''}$ = 5.3 Hz, 1 H, 4′′-H), 3.79 (s, 3 H, $COOCH_3$), 3.48 (dd, $J_{5b',4'}$ = 1.1, $J_{5b',5a'}$ = 10.3 Hz, 1 H, 5b′-H), 2.22 (s, 3 H, $NHCOCH_3$), 2.13 (s, 3 H, $OCOCH_3$), 2.11 (s, 3 H, $OCOCH_3$), 2.0 (s, 3 H, $OCOCH_3$), 1.54 [s, 3 H, $C(CH_3)_a$], 1.34 [s, 3 H, $C(CH_3)_b$] ppm. ^{13}C NMR ($CDCl_3$): δ = 171.4 ($NHCOCH_3$ at C-4), 170.8 (CH_3COO at C-9′′), 170.5 (CH_3COO at C-8′′), 169.5 (CH_3COO at C-7′′), 163.9 (C-4), 161.9 (C-1′′), 157.3 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 154.4 (C-2), 148.8 (C-6), 145.5 (C-2′′), 119.0–110.0 (CF_3), 114.1 [$C(CH_3)_2$], 106.3 (C-3′′), 99.3 (C-5), 97.1 (C-1′), 88.0 (C-4′), 83.8 (C-2′), 80.0 (C-3′), 72.8 (C-6′′), 72.5 (C-8′′), 69.0 (C-7′′), 68.7 (C-5′), 67.1 (C-4′′), 62.9 (C-9′), 52.5 ($COOCH_3$), 46.7 (C-5′′), 27.2 [$C(CH_3)_2$], 24.8 [$C(CH_3)_2$], 24.6 ($NHCOCH_3$ at C-4), 21.3, 20.8, 20.6 (3 C, $OCOCH_3$) ppm. MS (ESI$^+$): *m*/*z* = 793.7 [M + H]$^+$, 816.6 [M + Na]$^+$. $C_{32}H_{39}F_3N_4O_{16}$ (792.66): calcd. C 48.49, H 4.96, N 7.07; found C 48.71, H 4.70, N 6.98.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-4-*O*-(4-chlorophenyl)-3,5-dideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (18b): 18b (80 mg, 67%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with 4-chlorophenol (347 μL), heating for 60 min at 40 °C in CH_2Cl_2, m.p. 129–131 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –63.1 (*c* = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.33–7.28 (overlapping, 2 H, Ph), 6.91–6.87 (overlapping, 2 H, Ph), 6.84 (d, $J_{NH,5}$ = 9.0 Hz, 1 H, N-H), 6.25 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.54 (dd, $J_{7,6}$ = 2.0, $J_{7,8}$ = 4.8 Hz, 1 H, 7-H), 5.40 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$ = 4.8, $J_{8,9b}$ = 6.9 Hz, 1 H, 8-H), 4.78 (dd, $J_{4,5}$ = 3.7, $J_{4,3}$ = 5.3 Hz, 1 H, 4-H), 4.75 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.5 Hz, 1 H, 9a-H), 4.65–4.56 (overlapping, 2 H, 5-H and 6-H), 4.21 (dd, $J_{9b,8}$ = 6.9, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 3.83 (s, 3 H, $COOCH_3$), 2.14 (s, 3 H, $OCOCH_3$), 2.12 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.3, 169.7 (3 C, $OCOCH_3$), 161.4 (C-1), 157.2 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 154.9 (Ph), 146.5 (C-2), 129.9, 117.5 (5 C, Ph), 119.0–105.5 (CF_3), 104.9 (C-3), 73.0 (C-6), 71.2 (C-8), 67.9 (C-7), 67.5 (C-4), 62.0 (C-9), 52.8 ($COOCH_3$), 46.2 (C-5), 20.9, 20.7, 20.5 (3 C, CH_3COO) ppm. MS (ESI$^+$): *m*/*z* = 596.4 [M + H]$^+$, 618.6 [M + Na]$^+$. $C_{24}H_{25}ClF_3NO_{11}$ (595.90): calcd. C 48.37, H 4.23, N 2.35; found C 48.41, H 4.20, N 2.61.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*O*-(4-methoxyphenyl)-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (19a): Glycal **19a** (66 mg, 56%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with 4-chlorophenol (347 μL), heating for 60 min at 40 °C in CH_2Cl_2, m.p. 116–118 °C. $[\alpha]_D^{20}$ = +21.7 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.93–6.86 (overlapping, 4 H, Ph), 6.66 (d, $J_{NH,5}$ = 7.9 Hz, 1 H, N-H), 6.10 (d, $J_{3,4}$ = 2.5 Hz, 1 H, 3-H), 5.43 (dd, $J_{7,6}$ = 2.1, $J_{7,8}$ = 4.5 Hz, 1 H, 7-H), 5.35 (ddd, $J_{8,9a}$ = 2.7, $J_{8,7}$ = 4.5, $J_{8,9b}$ = 7.2 Hz, 1 H, 8-H), 4.77 (dd, $J_{9a,8}$ = 2.7, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.58 (dd, $J_{6,7}$ = 2.1, $J_{6,5}$ = 9.7 Hz, 1 H, 6-H), 4.35 (dd, $J_{4,3}$ = 2.5, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 4.19 (dd, $J_{9b,8}$ = 7.2, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 4.08–4.01 (m, 1 H, 5-H), 3.81 (s, 3 H, $COOCH_3$), 2.23 (s, 3 H, PhCH_3), 2.09 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.8, 170.6, 170.2 (3 C, O*C*OCH_3), 162.2 (C-1), 157.5 (q, $J_{C,F}$ = 38 Hz, *C*OCF_3), 151.4 (Ph), 144.2 (C-2), 130.7, 129.5, 128.9, 124.6, 115.2 (5 C, Ph), 119.0–105.5 (CF_3), 113.4 (C-3), 76.9 (C-6), 71.5 (C-8), 68.2 (C-7), 62.3 (C-9), 52.4 (COO*C*H_3), 51.0 (C-5), 37.2 (C-4), 20.9 (Ph*C*H_3), 20.7, 20.5 (3 C, *C*H_3COO) ppm. MS (ESI^+): *m*/*z* = 592.5 $[M + H]^+$, 514.5 $[M + Na]^+$. $C_{25}H_{28}F_3NO_{12}$ (575.49): calcd. C 50.18, H 4.90, N 2.43; found C 50.11, H 4.84, N 2.39.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-ethyl-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (20a) and Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-ethyl-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (20b)

Method 1: Starting from glycal **4** (105 mg, 0.2 mmol) and EtSH (148 μL), and heating for 15 min at 40 °C in CH_2Cl_2, a mixture of glycals **20a** and **20b** was obtained. This mixture was separated by flash chromatography, eluting with hexane/EtOAc (80:20 v/v), to give less polar glycal **20b** (30 mg, 28%), followed by more polar glycal **20a** (60 mg, 57%), both in pure form.

Data for Glycal 20a: M.p. 121–123 °C. $[\alpha]_D^{20}$ = +33.5 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.70 (d, $J_{NH,5}$ = 9.0 Hz, 1 H, N-H), 6.13 (d, $J_{3,4}$ = 3.0 Hz, 1 H, 3-H), 5.45 (dd, $J_{7,6}$ = 2.8, $J_{7,8}$ = 5.6 Hz, 1 H, 7-H), 5.37 (ddd, $J_{8,9a}$ = 2.9, $J_{8,7}$ = 5.6, $J_{8,9b}$ = 6.3 Hz, 1 H, 8-H), 4.63 (dd, $J_{9a,8}$ = 2.9, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.39 (dd, $J_{6,7}$ = 2.8, $J_{6,5}$ = 6.4 Hz, 1 H, 6-H), 4.19 (dd, $J_{9b,8}$ = 6.3, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 4.02–3.94 (m, 1 H, 5-H), 3.81 (s, 3 H, $COOCH_3$), 3.70 (dd, $J_{4,3}$ = 3.0, $J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 2.64–2.55 (overlapping, 2 H, SCH_2CH_3), 2.14 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$), 1.25 (t, $J_{CH3,CH2S}$ = 7.4 Hz, 3 H, SCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.3, 170.0 (3 C, O*C*OCH_3), 161.6 (C-1), 157.4 (q, $J_{C,F}$ = 38 Hz, *C*OCF_2), 144.0 (C-2), 119.0–110.0 (CF_3), 112.1 (C-3), 75.7 (C-6), 70.4 (C-8), 68.0 (C-7), 61.8 (C-9), 52.5 (COO*C*H_3), 49.0 (C-5), 42.1 (C-4), 23.9 (S*C*H_2CH_3), 20.8, 20.6 (3 C, O*C*OCH_3), 14.5 (SCH_2CH_3) ppm. MS (ESI^+): *m*/*z* = 530.6 $[M + H]^+$, 552.5 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.51, H 5.05, N 2.77.

Data for Glycal 20b: M.p. 133–135 °C. $[\alpha]_D^{20}$ = –29.9 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.85 (d, $J_{NH,5}$ = 10.0 Hz, 1 H, N-H), 6.20 (d, $J_{3,4}$ = 5.4 Hz, 1 H, 3-H), 5.46 (dd, $J_{7,6}$ = 2.8, $J_{7,8}$ = 5.0 Hz, 1 H, 7-H), 5.32 (ddd, $J_{8,9a}$ = 3.0, $J_{8,7}$ = 5.0, $J_{8,9b}$ = 6.7 Hz, 1 H, 8-H), 4.65 (dd, $J_{9a,8}$ = 3.0, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.62–4.56 (m, 1 H, 5-H), 4.19–4.13 (overlapping, 2 H, 9b-H and 6-H), 3.80 (s, 3 H, $COOCH_3$), 3.54 (dd, $J_{4,3}$ = $J_{4,5}$ = 5.4 Hz, 1 H, 4-H), 2.67–2.54 (overlapping, 2 H, SCH_2CH_3), 2.10 (s, 3 H, $OCOCH_3$), 2.08 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$) 1.29 (t, $J_{CH3,CH2S}$ = 7.4 Hz, 3 H, SCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1, 169.7 (3 C, O*C*OCH_3), 161.6 (C-1), 156.8 (q, $J_{C,F}$ = 38 Hz, *C*OCF_3), 143.0 (C-2), 119.0–110.0 (CF_3), 109.6 (C-3), 73.8 (C-6), 70.8 (C-8), 67.6 (C-7), 61.9 (C-9), 52.5 (COO*C*H_3), 45.9 (C-5), 42.2 (C-4), 28.7 (S*C*H_2CH_3), 20.9, 20.7, 20.5 (3 C, O*C*OCH_3), 15.1 (SCH_2CH_3) ppm. MS (ESI^+): *m*/*z* = 530.8 $[M + H]^+$, 552.1 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.21, H 5.01, N 2.73.

Method 2: Glycals **20a** and **20b** were also obtained by treating glycal **4** (105 mg, 0.2 mmol) in CH_2Cl_2 (1.5 mL) with EtSH (148 μL) and $BF_3{\cdot}Et_2O$ (25 μL, 0.2 mmol), at 25 °C for 48 h. After this time, the starting glycal had completely disappeared, and after general work-up, ^1H NMR spectroscopic analysis of the crude product showed a mixture of the major regioisomers as a pair of diastereomers (i.e., **20a** and **20b**; α/β, 2.3:1) and of their parent sialosides, the minor regioisomers, as a pair of diastereomers (i.e., **28a** and **28b**; α/β, 2.3:1). The crude mixture of thioglycoside **28a**, **28b**, **30a**, and **30b** showed: MS (ESI^+): *m*/*z* = 530.6 $[M + H]^+$, 552.8 $[M + Na]^+$.

i) Flash chromatography, eluting with hexane/EtOAc (80:20 v/v), first gave less polar glycal **20b** as an inseparable mixture together with parent sialosides **28a** and **28b** (46 mg, 43%; based on ^1H NMR spectroscopy), then more polar glycal **20a** (39 mg, 37%), in pure form, as a white solid.

Data for Glycal 20a: MS (ESI^+): *m*/*z* = 530.5 $[M + H]^+$, 552.2 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.45, H 5.01, N 2.74. All other physico-chemical properties were practically identical to those previously reported.

ii) Alternatively, on heating the reaction mixture of thioglycosides **28a**, **28b**, **30a**, and **30b** for 15 min at 40 °C in CH_2Cl_2, a mixture of glycals **20a** and **20b** was obtained that, after flash chromatography, eluting with hexane/EtOAc (80:20 v/v), gave less polar glycal **20b** (27 mg, 26%), followed by more polar glycal **20a** (55 mg, 54%), both in pure form.

Data for Glycal 20a: MS (ESI^+): *m*/*z* = 530.3 $[M + H]^+$, 552.26 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.40, H 4.87, N 2.60.

Data for Glycal 20b: MS (ESI^+): *m*/*z* = 530.0 $[M + H]^+$, 552.23 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.45, H 4.99, N 2.62. All other physico-chemical properties were practically identical to those previously reported.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-octyl-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (21a): Glycal **21a** (75 mg, 61%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with 1-octanethiol (347 μL), heating for 30 min at 40 °C in CH_2Cl_2, m.p. 109–111 °C. $[\alpha]_D^{20}$ = +46.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.86 (d, $J_{NH,5}$ = 9.1 Hz, 1 H, N-H), 6.11 (d, $J_{3,4}$ = 2.9 Hz, 1 H, 3-H), 5.45 (dd, $J_{7,6}$ = 2.6, $J_{7,8}$ = 5.2 Hz, 1 H, 7-H), 5.33 (ddd, $J_{8,9a}$ = 2.9, $J_{8,7}$ = 5.2, $J_{8,9b}$ = 6.7 Hz, 1 H, 8-H), 4.67 (dd, $J_{9a,8}$ = 2.9, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.37 (dd, $J_{6,7}$ = 2.6, $J_{6,5}$ = 9.3 Hz, 1 H, 6-H), 4.17 (dd, $J_{9b,8}$ = 6.7, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 4.00–3.95 (m, 1 H, 5-H), 3.81 (s, 3 H, $COOCH_3$), 3.66 (dd, $J_{4,3}$ = 2.9, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 2.60–2.47 [overlapping, 2 H, SC$H_2(CH_2)_6CH_3$], 2.13 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.04 (s, 3 H, $OCOCH_3$), 1.58–1.50 [overlapping, 2 H, $SCH_2CH_2(CH_2)_5CH_3$], 1.38–1.22 [overlapping, 10 H, $SCH_2CH_2(CH_2)_5CH_3$], 0.87 [t, $J_{CH3,CH2(CH2)6S}$ = 7.4 Hz, 3 H, $S(CH_2)_7CH_3$] ppm. ^{13}C NMR ($CDCl_3$): δ = 170.8, 170.3, 170.2 (3 C, O*C*OCH_3), 161.6 (C-1), 157.4 (q, $J_{C,F}$ = 38 Hz, *C*OCF_3), 144.0 (C-2), 119.0–110.0 (CF_3), 112.4 (C-3), 75.9 (C-6), 70.7 (C-8), 68.0 (C-7), 61.9 (C-9), 52.5 (COO*C*H_3), 48.7 (C-5), 42.4 (C-4), 31.8 [S*C*$H_2(CH_2)_6CH_3$], 29.6, 29.4, 29.1, 28.8, 22.6 [6 C, $SCH_2(CH_2)_6CH_3$], 20.8, 20.6, (3 C, O*C*OCH_3), 14.0 [$S(CH_2)_7CH_3$]

ppm. MS (ESI$^+$): m/z = 614.5 [M + H]$^+$, 636.6 [M + Na]$^+$. $C_{26}H_{38}F_3NO_{10}S$ (613.64): calcd. C 50.89, H 6.24, N 2.28; found C 50.01, H 6.13, N 2.17.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-phenyl-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (22a) and Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-phenyl-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (22b): Starting from glycal **4** (105 mg, 0.2 mmol) and PhSH (205 μL), after heating for 15 min at 40 °C in CH_2Cl_2, a mixture of glycals **22a** and **22b** was obtained. This was separated by flash chromatography, eluting with hexane/EtOAc (80:20 v/v), to give less polar glycal **22b** (16 mg, 14%), followed by more polar glycal **22a** (81 mg, 70%), both in pure form.

Data for Glycal 22a: M.p. 111–112 °C. $[\alpha]_D^{20}$ = +44.1 (c = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.51–7.46 (overlapping, 2 H, SPh), 7.35–7.29 (overlapping, 3 H, SPh), 7.12 (d, $J_{NH,5}$ = 9.1 Hz, 1 H, N-H), 6.15 (d, $J_{3,4}$ = 2.7 Hz, 1 H, 3-H), 5.36 (dd, $J_{7,6}$ = 1.8, $J_{7,8}$ = 5.1 Hz, 1 H, 7-H), 5.24 (ddd, $J_{8,9a}$ = 2.6, $J_{8,7}$ = 5.1, $J_{8,9b}$ = 7.0 Hz, 1 H, 8-H), 4.68 (dd, $J_{9a,8}$ = 2.6, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.32 (dd, $J_{6,7}$ = 1.8, $J_{6,5}$ = 10.0 Hz, 1 H, 6-H), 4.12 (dd, $J_{9b,8}$ = 7.0, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 4.02 (dd, $J_{4,3}$ = 2.7, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.94–3.87 (m, 1 H, 5-H), 3.76 (s, 3 H, $COOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.02 (overlapping, 6 H, 2 $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.9, 170.4 (3 C, O*C*OCH$_3$), 161.6 (C-1), 157.4 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 144.1 (C-2), 134.7, 129.2, 129.0 (6 C, SPh), 119.0–110.0 (CF_3), 111.8 (C-3), 75.6 (C-6), 70.9 (C-8), 67.8 (C-7), 61.9 (C-9), 52.5 ($COOCH_3$), 48.9 (C-4), 46.0 (C-5), 20.8, 20.6 (3 C, OCO*C*H$_3$) ppm. MS (ESI$^+$): m/z = 578.3 [M + H]$^+$, 600.5 [M + Na]$^+$. $C_{24}H_{26}F_3NO_{10}S$ (577.52): calcd. C 49.91, H 4.54, N 2.43; found C 50.07, H 4.63, N 2.53.

Data for Glycal 22b: M.p. 144–146 °C. $[\alpha]_D^{20}$ = –35.3 (c = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.41–7.28 (5 H, overlapping, SPh), 6.71 (d, $J_{NH,5}$ = 10.1 Hz, 1 H, N-H), 6.30 (d, $J_{3,4}$ = 5.6 Hz, 1 H, 3-H), 5.47 (dd, $J_{7,6}$ = 2.6, $J_{7,8}$ = 5.1 Hz, 1 H, 7-H), 5.33 (ddd, $J_{8,9a}$ = 3.0, $J_{8,7}$ = 5.1, $J_{8,9b}$ = 6.7 Hz, 1 H, 8-H), 4.68–4.62 (overlapping, 2 H, 9a-H and 5-H), 4.31 (dd, $J_{6,7}$ = 2.6, $J_{6,5}$ = 9.8 Hz, 1 H, 6-H), 4.19–4.12 (overlapping, 2 H, 9b-H and 4-H), 3.81 (s, 3 H, $COOCH_3$), 2.08 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1, 169.7 (3 C, O*C*OCH$_3$), 161.5 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 144.0 (C-2), 130.9, 129.8, 128.3 (6 C, SPh), 119.0–105.0 (CF_3), 108.3 (C-3), 73.6 (C-6), 70.8 (C-8), 67.5 (C-7), 61.9 (C-9), 52.6 ($COOCH_3$), 46.7 (C-5), 45.8 (C-4), 20.9, 20.7, 20.5 (3 C, OCO*C*H$_3$) ppm. MS (ESI$^+$): m/z = 578.2 [M + H]$^+$, 600.5 [M + Na]$^+$. $C_{24}H_{26}F_3NO_{10}S$ (577.52): calcd. C 49.91, H 4.54, N 2.43; found C 49.52, H 4.41, N 2.33.

Methyl 2-(*S*-2-Acetylamino-2-methoxycarbonylethyl)-7,8,9-tri-*O*-acetyl-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-2-thio-α-D-*manno*-non-3-en-2-ulopyranosidonate (23a): Thioglycoside **23a** (102 mg, 79%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with *N*-acetyl-L-cysteine methyl ester (71 mg, 0.4 mmol), heating for 60 min at 40 °C in CH_2Cl_2, m.p. 141–143 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = +19.4 (c = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.81 (d, $J_{NH,5}$ = 9.1 Hz, 1 H, 1 H, N-H), 6.37–6.29 (overlapping, 2 H, 3-H and CHN*H*Ac), 5.91 (dd, $J_{4,5}$ = 2.0, $J_{4,3}$ = 10.2 Hz, 1 H, 4-H), 5.33–5.28 (overlapping, 2 H, 7-H and 8-H), 4.94 (ddd, $J_{CH,CH2a}$ = 3.7, $J_{CH,CH2b}$ = $J_{CH,NH}$ = 9.6 Hz, 1 H, $CH_2CHNHAc$), 4.75–4.69 (m, 1 H, 5-H), 4.55 (dd, $J_{9a,8}$ = 2.3, $J_{9a,9b}$ = 12.5 Hz, 1 H, 9a-H), 4.48 (dd, $J_{6,7}$ = 1.8, $J_{6,5}$ = 10.0 Hz, 1 H, 6-H), 4.19 (dd, $J_{9b,8}$ = 6.2, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 3.84 (s, 3 H, $COOCH_3$), 3.78 (s, 3 H, $COOCH_3$), 3.28 (dd, $J_{CHa,CH}$ = 3.7, $J_{CHa,CHb}$ = 14.4 Hz, 1 H, SCH_{2a}CH), 2.84 (dd, $J_{CHb,CH}$ = 9.6, $J_{CHb,CHa}$ = 14.4 Hz, 1 H, SCH_{2b}CH), 2.14 (s, 3 H, $OCOCH_3$), 2.10 (overlapping, 6 H, 2 $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.8 (NH*C*OCH$_3$), 170.7 (*C*OOMe), 170.7, 170.3, 169.8 (3 C, O*C*OCH$_3$), 167.7 (C-1), 157.4 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 130.1 (C-4), 126.4 (C-3), 119.0–110.0 (CF_3), 84.2 (C-2), 70.6 (C-6), 70.2 (C-8), 68.4 (C-7), 62.4 (C-9), 53.3 (CHCOO*C*H$_3$), 52.8 ($COOCH_3$), 51.2 (*C*HCOOCH$_3$), 43.3 (C-5), 33.6 (S*C*H$_2$CH), 23.0 (*C*H$_3$CONH), 21.0, 20.7, 20.5 (3 C, OCO*C*H$_3$) ppm. MS (ESI$^+$): m/z = 645.5 [M + H]$^+$, 667.5 [M + Na]$^+$. $C_{24}H_{31}F_3N_2O_{13}S$ (644.57): calcd. C 44.72, H 4.85, N 4.35; found C 44.15, H 4.32, N 4.09.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-3-enonate (24a): Cyclic ether **24a** (81 mg, 86%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with triethylsilane (319 μL), heating for 15 min at 40 °C in CH_2Cl_2, m.p. 108–110 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = +34.2 (c = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 6.89 (d, $J_{NH,5}$ = 8.6 Hz, 1 H, N-H), 6.04 (ddd, $J_{3,5}$ = $J_{3,2}$ = 2.2, $J_{3,4}$ = 10.3 Hz, 1 H, 3-H), 5.82 (ddd, $J_{4,5}$ = $J_{4,2}$ = 2.5, $J_{4,3}$ = 10.3 Hz, 1 H, 4-H), 5.41 (ddd, $J_{8,9a}$ = 2.3, $J_{8,7}$ = $J_{8,9b}$ = 6.2 Hz, 1 H, 8-H), 5.25 (dd, $J_{7,6}$ = 2.0, $J_{7,8}$ = 6.2 Hz, 1 H, 7-H), 4.82–4.78 (m, 1 H, 2-H), 4.50 (dd, $J_{9a,8}$ = 2.3, $J_{9a,9b}$ = 12.5 Hz, 1 H, 9a-H), 4.45–4.39 (m, 1 H, 5-H), 4.21 (dd, $J_{9b,8}$ = 6.2, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 3.92 (dd, $J_{6,7}$ = 2.0, $J_{6,5}$ = 9.3 Hz, 1 H, 6-H), 3.77 (s, 3 H, $COOCH_3$), 2.13 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.02 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1 (3 C, O*C*OCH$_3$), 168.4 (C-1), 157.1 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 127.6 (C-4), 126.3 (C-3), 119.0–110.0 (CF_3), 74.8 (C-2), 73.8 (C-6), 70.1 (C-8), 68.4 (C-7), 62.3 (C-9), 52.6 ($COOCH_3$), 44.6 (C-5), 20.8, 20.6 (3 C, OCO*C*H$_3$) ppm. MS (ESI$^+$): m/z = 470.4 [M + H]$^+$, 492.3 [M + Na]$^+$. $C_{18}H_{22}F_3NO_{10}$ (469.36): calcd. C 46.06, H 4.72, N 2.98; found C 46.18, H 4.22, N 3.00.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-4-chloro-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (25a) and Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-4-chloro-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (25b): Starting from glycal **4** (105 mg, 0.2 mmol) and TMSCl (254 μL, 2.0 mmol), heating for 15 min at 40 °C in CH_2Cl_2, a mixture of glycals **25b** and **25a** was obtained. This was separated by rapid chromatography, eluting with hexane/EtOAc (80:20 v/v), to give less polar glycal **25b** (55 mg, 19.5%), followed by more polar glycal **25a** (18 mg, 58.5%), both in pure form.

Data for Glycal 25a: M.p. 115–117 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = +51.2 (c = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 7.18 (d, $J_{NH,5}$ = 8.6 Hz, 1 H, N-H), 6.07 (d, $J_{3,4}$ = 2.5 Hz, 1 H, 3-H), 5.39 (dd, $J_{7,6}$ = 1.6, $J_{7,8}$ = 5.6 Hz, 1 H, 7-H), 5.31 (ddd, $J_{8,9a}$ = 2.6, $J_{8,7}$ = $J_{8,9b}$ = 6.0 Hz, 1 H, 8-H), 4.99 (dd, $J_{4,3}$ = 2.5, $J_{4,5}$ = 8.9 Hz, 1 H, 4-H), 4.65 (dd, $J_{9a,8}$ = 2.6, $J_{9a,9b}$ = 12.5 Hz, 1 H, 9a-H), 4.53 (dd, $J_{6,7}$ = 1.6, $J_{6,5}$ = 10.4 Hz, 1 H, 6-H), 4.18 (dd, $J_{9b,8}$ = 6.0, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 4.07–4.00 (m, 1 H, 5-H), 3.82 (s, 3 H, $COOCH_3$), 2.15 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$), 2.04 (s, 3 H, OCO CH_3), ppm. ^{13}C NMR ($CDCl_3$): δ = 170.8, 170.5, 170.2 (3 C, O*C*OCH$_3$), 161.2 (C-1), 157.5 (q, $J_{C,F}$ = 38 Hz, *C*OCF$_3$), 144.3 (C-2), 119.0–110.0 (CF_3), 110.1 (C-3), 75.3 (C-6), 70.4 (C-8), 67.6 (C-7), 61.7 (C-9), 52.9 (C-4), 52.7 (COO*C*H$_3$), 52.5 (C-5), 20.8, 20.6 (3 C, OCO*C*H$_3$) ppm. MS (ESI$^+$): m/z = 504.7 [M + H]$^+$, 526.7 [M + Na]$^+$. $C_{18}H_{21}ClF_3NO_{10}$ (503.81): calcd. C 42.91, H 4.20, N 2.78; found C 42.11, H 4.01, N 2.47.

Data for Glycal 25b: M.p. 109–111 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –19.3 (c = 1 in $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 6.71 (d, $J_{NH,5}$ = 9.6 Hz, 1 H, N-H), 6.23 (d, $J_{3,4}$ = 5.6 Hz, 1 H, 3-H), 5.47 (dd, $J_{7,6}$ = 2.1, $J_{7,8}$ = 5.4 Hz, 1 H, 7-H), 5.36 (ddd, $J_{8,9a}$ = 2.8, $J_{8,7}$

= 5.4, $J_{8,9b}$ = 6.4 Hz, 1 H, 8-H), 4.74 (dd, $J_{4,5}$ = 4.0, $J_{4,3}$ = 5.6 Hz, 1 H, 4-H), 4.73–4.67 (m, 1 H, 5-H), 4.66 (dd, $J_{9a,8}$ = 2.8, $J_{9a,9b}$ = 12.5 Hz, 1 H, 9a-H), 4.52 (dd, $J_{6,7}$ = 2.1, $J_{6,5}$ = 10.0 Hz, 1 H, 6-H), 4.15 (dd, $J_{9b,8}$ = 6.4, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 3.83 (s, 3 H, $COOCH_3$), 2.10 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.1, 169.6 (3 C, $OCOCH_3$), 161.2 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.3 (C-2), 119.0–110.0 (CF_3), 107.8 (C-3), 72.6 (C-6), 70.7 (C-8), 67.2 (C-7), 61.8 (C-9), 53.8 (C-4), 52.8 ($COOCH_3$), 46.4 (C-5), 20.8, 20.7, 20.5 (3 C, $OCOCH_3$) ppm. MS (ESI^+): *m*/*z* = 504.8 $[M + H]^+$, 526.7 $[M + Na]^+$. $C_{18}H_{21}ClF_3NO_{10}$ (503.81): calcd. C 42.91, H 4.20, N 2.78; found C 42.01, H 3.98, N 2.42.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-4-bromo-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (26b): Glycal **26b** (80 mg, 73%) was obtained as a white solid by the reaction of glycal **4** (105 mg, 0.2 mmol) with bromotrimethylsilane (319 μL), heating for 30 min at 40 °C in CH_2Cl_2, m.p. 103–105 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –23.4 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.75 (d, $J_{NH,5}$ = 9.6 Hz, 1 H, N-H), 6.31 (d, $J_{3,4}$ = 5.9 Hz, 1 H, 3-H), 5.47 (dd, $J_{7,6}$ = 2.0, $J_{7,8}$ = 6.0 Hz, 1 H, 7-H), 5.37 (ddd, $J_{8,9a}$ = 2.6, $J_{8,7}$ = $J_{8,9b}$ = 6.0 Hz, 1 H, 8-H), 4.91 (dd, $J_{4,5}$ = 4.0, $J_{4,3}$ = 5.9 Hz, 1 H, 4-H), 4.69–4.61 (overlapping, 2 H, 9a-H and 6-H), 4.55–4.49 (m, 1 H, 5-H), 4.15 (dd, $J_{9b,8}$ = 6.0, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 3.82 (s, 3 H, $COOCH_3$), 2.10 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.7, 170.1, 169.6 (3 C, $OCOCH_3$), 161.1 (C-1), 157.0 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 144.7 (C-2), 119.0–110.0 (CF_3), 109.1 (C-3), 73.4 (C-6), 70.7 (C-8), 67.3 (C-7), 61.9 (C-9), 52.8 ($COOCH_3$), 47.2 (C-4), 45.8 (C-5), 20.8, 20.7, 20.5 (3 C, $OCOCH_3$) ppm. MS (ESI^+): *m*/*z* = 549.3 $[M + H]^+$, 571.2 $[M + Na]^+$. $C_{18}H_{21}BrF_3NO_{10}$ (548.26): calcd. C 39.43, H 3.86, N 2.55; found C 38.88, H 3.56, N 2.31.

Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-(*S*-2-acetylamino-2-methoxycarbonylethyl)-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*galacto*-non-2-enonate (27a) and Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-dideoxy-4-*S*-(S-2-acetylamino-2-methoxycarbonylethyl)-4-thio-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (27b): Starting from glycal **23a** (50 mg, 0.08 mmol) in CH_2Cl_2, and treating with $BF_3{\cdot}Et_2O$ (492 μL, 4.0 mmol) for 2 h at 40 °C, a mixture of glycals **27b** and **27a** was obtained. It was separated by flash chromatography, eluting with hexane/EtOAc (50:50 v/v), to give less polar glycal **27b** (27 mg, 53%), followed by more polar glycal **27a** (14 mg, 27%), both in pure form.

Data for Glycal 27a: M.p. 160–162 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = +42.7 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 7.68 (br. s, 1 H, N-H), 6.33 (d, $J_{NH,CH}$ = 9.0 Hz, 1 H, CHN*H*Ac), 6.04 (d, $J_{3,4}$ = 1.8 Hz, 1 H, 3-H), 5.45 (dd, $J_{7,6}$ = 2.3, $J_{7,8}$ = 5.9 Hz, 1 H, 7-H), 5.37 (ddd, $J_{8,9a}$ = 2.7, $J_{8,7}$ = $J_{8,9b}$ = 5.9 Hz, 1 H, 8-H), 4.76 (ddd, $J_{CH,CHa}$ = 4.8, $J_{CH,CHb}$ = 7.6 $J_{CH,NH}$ = 9.0 Hz, 1 H, $CH_2CHNHAc$), 4.60–4.53 (overlapping, 2 H, 9a-H and 6-H), 4.18 (dd, $J_{9b,8}$ = 5.9, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.89–3.83 (overlapping, 2 H, 5-H and 4-H), 3.82 (s, 3 H, $COOCH_3$), 3.77 (s, 3 H, $COOCH_3$), 3.03 (dd, $J_{CH2a,CH}$ = 4.8, $J_{CH2a,CH2b}$ = 14.2 Hz, 1 H, $SCH_{2a}CH$), 2.84 (dd, $J_{CH2b,CH}$ = 7.6, $J_{CH2b,CH2a}$ = 14.2 Hz, 1 H, $SCH_{2b}CH$), 2.13 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, OCO CH_3), 2.06 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $NHCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.9 ($NHCOCH_3$), 170.8 ($COOMe$), 170.7, 170.1, 170.0 (3 C, $OCOCH_3$), 161.6 (C-1), 157.9 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 145.5 (C-2), 119.0–110.0 (CF_3), 111.2 (C-3), 75.9 (C-6), 70.2 (C-8), 67.7 (C-7), 61.9 (C-9), 53.0 ($CHCOOCH_3$), 52.6 ($COOCH_3$), 51.9 ($CHCOOCH_3$), 49.9 (C-5), 42.6 (C-4), 31.8 (SCH_2CH), 23.1 (CH_3CONH), 20.9, 20.7, 20.6 (3 C, CH_3COO) ppm. MS (ESI^+): *m*/*z* = 645.6 $[M + H]^+$, 668.5 $[M + Na]^+$. $C_{24}H_{31}F_3N_2O_{13}S$ (644.57): calcd. C 44.72, H 4.85, N 4.35; found C 45.31, H 4.78, N 4.37.

Data for Glycal 27b: M.p. 156–158 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –38.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 7.75 (d, $J_{NH,5}$ = 9.6 Hz, 1 H, N-H), 6.33 (d, $J_{NH,CH}$ = 7.6 Hz, 1 H, CHN*H*Ac), 6.10 (d, $J_{3,4}$ = 5.3 Hz, 1 H, 3-H), 5.48 (dd, $J_{7,6}$ = 2.8, $J_{7,8}$ = 4.8 Hz, 1 H, 7-H), 5.35 (ddd, $J_{8,9a}$ = 3.1, $J_{8,7}$ = 4.8, $J_{8,9b}$ = 6.9 Hz, 1 H, 8-H), 4.84 (ddd, $J_{CH,CH2a}$ = 4.9, $J_{CH,CH2b}$ = 6.3, $J_{CH,NH}$ = 7.6 Hz, 1 H, $CH_2CHNHAc$), 4.66–4.58 (overlapping, 2 H, 9a-H and 5-H), 4.26 (dd, $J_{6,7}$ = 2.8, $J_{6,5}$ = 9.7 Hz, 1 H, 6-H), 4.17 (dd, $J_{9b,8}$ = 6.9, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.80 (overlapping, 6 H, 2 $COOCH_3$), 3.66 (dd, $J_{4,3}$ = $J_{4,5}$ = 5.3 Hz, 1 H, 4-H), 3.14 (dd, $J_{CH2a,CH}$ = 4.8, $J_{CH2a,CH2b}$ = 14.1 Hz, 1 H, $SCH_{2a}CH$), 2.97 (dd, $J_{CHb,CH}$ = 6.3, $J_{CHb,CHa}$ = 14.1 Hz, 1 H, $SCH_{2b}CH$), 2.09 (s, 3 H, $OCOCH_3$), 2.08 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 2.06 (s, 3 H, $NHCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6 (2 C, $NHCOCH_3$ and $COOMe$), 170.4, 170.1, 169.7 (3 C, $OCOCH_3$), 161.5 (C-1), 157.4 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 143.4 (C-2), 119.0–110.0 (CF_3), 108.4 (C-3), 73.5 (C-6), 70.7 (C-8), 67.8 (C-7), 61.9 (C-9), 53.0 ($CHCOOCH_3$), 52.6 ($COOCH_3$), 52.4 ($CHCOOCH_3$), 46.4 (C-5), 44.0 (C-4), 36.9 (SCH_2CH), 23.0 ($NHCOCH_3$), 20.9, 20.7, 20.5 (3 C, $OCOCH_3$) ppm. MS (ESI^+): *m*/*z* = 645.6 $[M + H]^+$, 668.5 $[M + Na]^+$. $C_{24}H_{31}F_3N_2O_{13}S$ (644.57): calcd. C 44.72, H 4.85, N 4.35; found C 45.05, H 4.44, N 4.02.

Dimethyl 7,8,9-tri-*O*-acetyl-3,4,5-trideoxy-5-[(trifluoroacetyl)-amino]-α-D-*manno*-non-3-en-2-ulopyranosidonate (30a) and Dimethyl 7,8,9-tri-*O*-acetyl-3,4,5-trideoxy-5-[(trifluoroacetyl)amino]-α-D-*manno*-non-3-en-2-ulopyranosidonate (30b)

Method 1: Methyl ketoside **29b** (90 mg, 0.2 mmol), obtained according to the procedure of Ikeda et al.,[19] was *N*-transacylated in CH_3CN (0.6 mL) with TFAA (142 μL, 1.0 mmol) containing Et_3N (306 μL, 2.2 mmol)[16] to give sialoside **30b** (75 mg, 61%) in pure form as a white solid, m.p. 111–112 °C (CH_2Cl_2/diisopropyl ether). $[\alpha]_D^{20}$ = –36.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 5.95 (d, $J_{NH,5}$ = 9.0 Hz, 1 H, N-H), 5.93 (dd, $J_{4,5}$ = 2.5, $J_{4,3}$ = 10.1 Hz, 1 H, 3-H), 5.91 (dd, $J_{4,5}$ = 1.7, $J_{4,3}$ = 10.1 Hz, 1 H, 4-H), 5.35–5.30 (overlapping, 2 H, 7-H and 8-H), 4.58–4.52 (overlapping, 2 H, 9a-H and 5-H), 4.24 (dd, $J_{9b,8}$ = 5.3, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 4.19 (dd, $J_{6,7}$ = 2.0, $J_{6,5}$ = 10.3 Hz, 1 H, 6-H), 3.81 (s, 3 H, $COOCH_3$), 3.29 (s, 3 H, OCH_3), 2.15 (s, 3 H, $OCOCH_3$), 2.09 (s, 3 H, $OCOCH_3$), 2.04 (s, 3 H, $OCOCH_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.3, 170.1 (3 C, $OCOCH_3$), 167.2 (C-1), 157.2 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 131.3 (C-4), 126.9 (C-3), 119.0–110.0 (CF_3), 96.5 (C-2), 70.3 (C-6), 69.3 (C-8), 68.1 (C-7), 62.0 (C-9), 52.9 ($COOCH_3$), 51.1 (OCH_3), 44.2 (C-5), 20.8, 20.6, 20.5 (3 C, $OCOCH_3$) ppm. MS (ESI^+): *m*/*z* = 500.4 $[M + H]^+$, 522.4 $[M + Na]^+$. $C_{19}H_{24}F_3NO_{11}$ (499.39): calcd. C 45.70, H 4.84, N 2.80; found C 45.76, H 4.92, N 2.93.

Method 2: A mixture of methyl ketosides **29a** and **29b** (1:1.3 ratio; 90 mg, 0.2 mmol), obtained according to the procedure of Ikeda et al.,[19] was *N*-transacylated in CH_3CN (0.6 mL) with TFAA (142 μL, 1.0 mmol) containing Et_3N (306 μL, 2.2 mmol)[16] to give an inseparable mixture of glycosides **30a** and **30b** (1:1.3 ratio; 75 mg, 75%) in pure form as a white solid.

Data for Glycoside 30a, Minor Compound: ^1H NMR ($CDCl_3$): δ = 6.65 (d, $J_{NH,5}$ = 8.0 Hz, 1 H, N-H), 6.10 (dd, *J* = 2.0, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.91 (dd, *J* = 2.5, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.44 (ddd, $J_{8,9a}$ = 2.3, $J_{8,9b}$ = 4.9, $J_{8,7}$ = 7.5 Hz, 1 H, 1 H, 8-H), 5.27 (dd, $J_{7,6}$ = 2.0, $J_{7,8}$ = 7.5 Hz, 1 H, 7-H), 4.45–4.40 (overlapping, 2 H, 9a-H and 6-H), 4.38–4.27 (m, 1 H, 5-H), 4.24 (dd, $J_{9b,8}$ = 4.9, $J_{9b,9a}$ = 12.5 Hz, 1 H, 9b-H), 3.79 (s, 3 H, $COOCH_3$), 3.35

(s, 3 H, OCH_3), 2.14 (s, 3 H, $OCOCH_3$), 2.08 (s, 3 H, $OCOCH_3$), 2.04 (s, 3 H, $OCOCH_3$) ppm. The NMR signals of compound **30b** were practically identical to those above previously reported. Data for the mixture of glycosides **30a** and **30b**: MS (ESI^+): *m/z* = 522.4 $[M + Na]^+$, 1020.5 $[M + Na]^+$. $C_{19}H_{24}F_3NO_{11}$ (499.39): calcd. C 45.70, H 4.84, N 2.80; found C 45.70, H 4.95, N 2.90.

Methyl Oxazolo[5,4]-Fused 7,8,9-Tri-*O*-acetyl-2,3,4,5-tetradeoxy-2,3-didehydro-2,3-trideoxy-4,5-dihydro-2-trifluoromethyl-D-*glycero*-D-*talo*-non-2-enoate (31) and Methyl 7,8,9-Tri-*O*-acetyl-2,6-anhydro-3,5-diideoxy-5-[(trifluoroacetyl)amino]-D-*glycero*-D-*talo*-non-2-enonate (32)

BF_3·Et_2O Treatment of the Pure Glycoside 29b and of 29a and 29b Mixture: The reactions were performed separately on sialoside **29b** or on an inseparable mixture of glycosides **29a** and **29b** (100 mg, 0.2 mmol), dissolved in CH_2Cl_2 (1.5 mL), using MeOH (81 μL, 2.0 mmol) and BF_3·Et_2O (246 μL, 2.0 mmol) at 40 °C for 15 min. Then, the reaction mixtures were worked up:

i) as indicated in the General Remarks to give, after flash chromatography (EtOAc/hexane, 1:1 v/v), methyl oxazolo[5,4]-fused **31** (17 mg, 18%) together with compound **32** (31 mg, 58%).

Data for 31: MS (ESI^+): *m/z* = 568.7 $[M + H]^+$, 590.2 $[M + Na]^+$. $C_{18}H_{20}F_3NO_{10}$ (467.35): calcd. C 46.26, H 4.31, N 3.00; found C 46.32, H 4.40, N 2.92. All other physico-chemical properties were practically identical to those previously reported.

Data for 32: MS (ESI^+): *m/z* = 486.0 $[M + H]^+$, 508.4 $[M + Na]^+$. $C_{18}H_{22}F_3NO_{11}$ (485.37): calcd. C 44.54, H 4.57, N 2.89; found C 44.08, H 4.20, N 2.70. All other physico-chemical properties were practically identical to those previously reported.

ii) by the addition of water and extraction of the mixture with CH_2Cl_2 to give, after subsequent washing with ice-cold NaCl (aq.), drying, and solvent evaporation, a crude residue. Rapid chromatography (EtOAc/hexane, 1:1 v/v) gave compound **32** (76 mg, 78%). MS (ESI^+): *m/z* = 486.4 $[M + H]^+$, 508.7 $[M + Na]^+$, 1194.1 $[2M + Na]^+$. MS [ESI]: *m/z* = 484.1 [M – H]. $C_{18}H_{22}F_3NO_{11}$ (485.37): calcd. C 44.54, H 4.57, N 2.89; found C 44.11, H 4.23, N 2.76. All other physico-chemical properties were practically identical to those previously reported.

Ethyl Methyl 7,8,9-Tri-*O*-acetyl-3,4,5-trideoxy-2-thio-5-[(trifluoroacetyl)amino]-α-D-*manno*-non-3-en-2-ulopyranosidonate (28a) and Ethyl Methyl 7,8,9-Tri-*O*-acetyl-3,4,5-trideoxy-2-thio-5-[(trifluoroacetyl)amino]-β-D-*manno*-non-3-en-2-ulopyranosidonate (28b): A solution of oxazoline **5** (100 mg, 0.24 mmol) in CH_3CN (0.2 mL) was treated with EtSH (100 μL, 1.4 mmol) and $Bi(OTf)_3$ (5 mg, 0.07 mmol), following the procedure of Ikeda et al.,[19] to give a mixture of thioglycosides **33a** and **33b**. This was separated by rapid chromatography, eluting with hexane/EtOAc (80:20 v/v), to give less polar thioglycoside **33a** (38 mg, 33%), then more polar thioglycoside **33b** (59 mg, 52%).

Data for Thioglycosides 33a: M.p. 123–124 °C. $[\alpha]_D^{20}$ = –30.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.15 (dd, *J* = 2.4, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.78 (dd, *J* = 1.8, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.44 (d, $J_{NH,5}$ = 9.6 Hz, 1 H, N-H), 5.40 (dd, $J_{7,6}$ = 2.4, $J_{7,8}$ = 4.9 Hz, 1 H, 7-H), 5.25 (ddd, $J_{8,9a}$ = 2.4, $J_{8,7}$ = 4.9, $J_{8,9b}$ = 6.8 Hz, 1 H, 8-H), 4.68–4.58 (overlapping, 2 H, 9a-H and 5-H), 4.37 (dd, $J_{6,7}$ = 2.4, $J_{6,5}$ = 10.0 Hz, 1 H, 6-H), 4.28 (dd, $J_{9b,8}$ = 6.8, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.83 (s, 3 H, $COOCH_3$), 2.70–2.55 (overlapping, 2 H, SCH_2CH_3), 2.13 (s, 3 H, $OCOCH_3$), 2.08 (s, 3 H, $OCOCH_3$), 2.03 (s, 3 H, $OCOCH_3$), 1.96 (s, 3 H, CH_3CONH), 1.16 (t, 3 H, SCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.5 (CH_3CONH), 170.4, 170.2, 169.8 (3 C, $OCOCH_3$), 167.3 (C-1), 130.7 (C-4 or C-3), 126.4 (C-4 or C-3), 85.7 (C-2), 71.4 (C-8), 70.7 (C-6), 68.5 (C-7), 62.5 (C-9), 52.8 ($COOCH_3$), 43.1 (C-5), 24.4 (SCH_2CH_3), 23.3 ($NHCOCH_3$), 21.0, 20.7 (3 C, $OCOCH_3$), 14.1 (SCH_2CH_3) ppm. MS (ESI^+): *m/z* = 476.1 $[M + H]^+$, 498.5 $[M + Na]^+$. $C_{20}H_{29}NO_{10}S$ (475.51): calcd. C 50.52, H 6.15, N 2.95; found C 50.41, H 6.03, N 2.70.

Data for Thioglycoside 33b: M.p. 120–124 °C. $[\alpha]_D^{20}$ = –14.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 5.93 (dd, *J* = 2.5, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.86 (dd, *J* = 1.6, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.47–5.41 (overlapping, N-H and 8-H), 5.40 (dd, $J_{7,6}$ = 2.0, $J_{7,8}$ = 6.3 Hz, 1 H, 7-H), 4.54 (dd, $J_{9a,8}$ = 2.4, $J_{9a,9b}$ = 12.4 Hz, 1 H, 9a-H), 4.48–4.42 (m, 1 H, 5-H), 4.28 (dd, $J_{9b,8}$ = 5.9, $J_{9b,9a}$ = 12.4 Hz, 1 H, 9b-H), 3.94 (dd, $J_{6,7}$ = 1.9, $J_{6,5}$ = 9.8 Hz, 1 H, 6-H), 3.76 (s, 3 H, $COOCH_3$), 2.75–2.58 (overlapping, 2 H, SCH_2CH_3), 2.13 (s, 3 H, $OCOCH_3$), 2.11 (s, 3 H, $OCOCH_3$), 2.05 (s, 3 H, $OCOCH_3$), 1.97 (s, 3 H, CH_3CONH), 1.25 (t, 3 H, SCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.7 (CH_3CONH), 170.5, 170.2, 169.8 (3 C, $OCOCH_3$), 168.8 (C-1), 131.4 (C-4 or C-3), 126.5 (C-4 or C-3), 84.6 (C-2), 74.2 (C-8), 70.4 (C-6), 68.0 (C-7), 62.2 (C-9), 52.9 ($COOCH_3$), 43.2 (C-5), 23.4 (2 C, $NHCOCH_3$ and SCH_2CH_3), 21.2, 20.8, 20.7 (3 C, $OCOCH_3$), 14.5 (SCH_2CH_3) ppm. MS (ESI^+): *m/z* = 476.4 $[M + H]^+$, 498.7 $[M + Na]^+$. $C_{20}H_{29}NO_{10}S$ (475.51): calcd. C 50.52, H 6.15, N 2.95; found C 50.410, H 6.00, N 2.85.

Next, in separate experiments, methyl ketosides **33a** and **33b** (95 mg, 0.2 mmol) were *N*-transacylated in CH_3CN (0.6 mL) with TFAA (142 μL, 1.0 mmol) containing Et_3N (306 μL, 2.2 mmol),[16] to give thioglycosides **28a** (83 mg, 78%) and **28b** (85 mg, 81%), respectively, both in pure form as white solids.

Data for Thioglycoside 28a: M.p. 119–122 °C. $[\alpha]_D^{20}$ = –18.1 (*c* = 1 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 6.54 (br. s, 1 H, N-H), 6.21 (dd, $J_{3,5}$ = 1.5, $J_{3,4}$ = 10.1 Hz, 1 H, 3-H), 5.78 (dd, $J_{4,5}$ = 1.1, $J_{4,3}$ = 10.1 Hz, 1 H, 4-H), 5.31 (dd, $J_{7,6}$ = 1.3, $J_{7,8}$ = 6.1 Hz, 1 H, 7-H), 5.30–5.27 (m, 1 H, 8-H), 4.55 (dd, $J_{9a,8}$ = 2.4, $J_{9a,9b}$ = 12.6 Hz, 1 H, 9a-H), 4.50–4.47 (overlapping, 2 H, 5-H and 6-H), 4.28 (dd, $J_{9b,8}$ = 5.5, $J_{9b,9a}$ = 12.6 Hz, 1 H, 9b-H), 3.83 (s, 3 H, $COOCH_3$), 2.68–2.54 (overlapping, 2 H, SCH_2CH_3), 2.14 (s, 3 H, $OCOCH_3$), 2.11 (s, 3 H, $OCOCH_3$), 2.04 (s, 3 H, $OCOCH_3$), 1.18 (t, $J_{CH3,CH2S}$ = 7.4 Hz, 3 H, SCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.5, 170.4, 170.2 (3 C, $OCOCH_3$), 167.1 (C-1), 157.1 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 128.2 (C-4), 127.7 (C-3), 119.0–110.0 (CF_3), 85.9 (C-2), 70.4, (C-6), 69.3 (C-8), 68.3 (C-7), 62.1 (C-9), 53.0 ($COOCH_3$), 44.5 (C-5), 24.6 (SCH_2CH_3), 21.0, 20.7 (3 C, $OCOCH_3$), 14.0 (SCH_2CH_3) ppm. MS (ESI^+): *m/z* = 530.4 $[M + H]^+$, 552.5 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.31, H 4.90, N 2.60.

Data for Thioglycoside 28b: ^1H NMR ($CDCl_3$): δ = 6.56 (d, $J_{NH,5}$ = 8.5 Hz, 1 H, N-H), 6.07 (dd, *J* = 2.6, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.93 (dd, *J* = 1.7, *J* = 10.1 Hz, 1 H, 3-H or 4-H), 5.47 (ddd, $J_{8,9a}$ = 2.4, $J_{8,9b}$ = 4.8, $J_{8,7}$ = 7.3 Hz, 1 H, 8-H), 5.30 (dd, $J_{7,6}$ = 1.8, $J_{7,8}$ = 7.3 Hz, 1 H, 7-H), 4.55 (dd, $J_{9a,8}$ = 2.4, $J_{9a,9b}$ = 12.6 Hz, 1 H, 9a-H), 4.35–4.29 (overlapping, 2 H, 9b-H and 5-H), 4.11 (dd, $J_{6,7}$ = 1.8, $J_{6,5}$ = 9.8 Hz, 1 H, 6-H), 3.81 (s, 3 H, $COOCH_3$), 2.79–2.58 (overlapping, 2 H, SCH_2CH_3), 2.18 (s, 3 H, $OCOCH_3$), 2.16 (s, 3 H, $OCOCH_3$), 2.07 (s, 3 H, $OCOCH_3$), 1.28 (t, $J_{CH3,CH2S}$ = 7.4 Hz, 3 H, SCH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 170.7, 170.4 (3 C, $OCOCH_3$), 168.3 (C-1), 157.1 (q, $J_{C,F}$ = 38 Hz, $COCF_3$), 128.8 (C-3 or C-4), 127.7 (C-3 or C-4), 119.0–110.0 (CF_3), 84.9 (C-2), 72.7 (C-6), 69.4 (C-8), 67.9 (C-7), 61.9 (C-9), 53.1 ($COOCH_3$), 44.4 (C-5), 23.5 (SCH_2CH_3), 21.2, 20.7 (3 C, $OCOCH_3$), 14.5 (SCH_2CH_3) ppm. MS (ESI^+): *m/z* = 530.1 $[M + H]^+$, 552.0 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.31, H 4.90, N 2.60.

BF_3·Et_2O Equilibration of Pure Sialosides 28b and of 28a: The reactions were performed separately on starting sialosides **28a** and **28b** (105 mg, 0.2 mmol), dissolved in CH_2Cl_2 (1.5 mL), using EtSH (148 μL, 2.0 mmol) and BF_3·Et_2O (246 μL, 2.0 mmol) at 40 °C for 15 min. Then, the reaction mixtures were worked up as indicated in the General Remarks to give, after flash chromatography eluting with hexane/EtOAc (80:20 v/v), less polar glycal **20b** (28–34 mg, 26–30%), followed by more polar glycal **20a** (58–64 mg, 55–60%). both in pure form.

Data for Glycal 20a: MS (ESI^+): m/z = 530.2 $[M + H]^+$, 552.3 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.52, H 5.00, N 2.73. All other physico-chemical properties were practically identical to those previously reported.

Data for Glycal 20b: MS (ESI^+): m/z = 530.7 $[M + H]^+$, 552.9 $[M + Na]^+$. $C_{20}H_{26}F_3NO_{10}S$ (529.48): calcd. C 45.37, H 4.95, N 2.65; found C 45.30, H 4.83, N 2.60. All other physico-chemical properties were practically identical to those previously reported.

BF_3·Et_2O Equilibration of Pure Glycals 20b and 20a: The reactions were performed separately on the starting sialosides **20a** and **20b** (105 mg, 0.2 mmol), dissolved in CH_2Cl_2 (1.5 mL), using EtSH (148 μL, 2.0 mmol) and BF_3·Et_2O (246 μL, 2.0 mmol) at 40 °C for 15 min. Then, the reaction mixtures were worked up as indicated in the General Remarks to give, after flash chromatography eluting with hexane/EtOAc (80:20 v/v), only the starting material, unchanged and in pure form, with all the physico-chemical properties practically identical to those previously reported.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra.

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[27] The 2α or 2β stereochemistry of the Ferrier products was assigned taking into account the correct assignment of 2α and 2β methyl ketosides **29a** and **29b** in: J. Maudrin, B. Barrere, B. Chantegrel, C. Deshayes, G. Quash, A. Doutheau, *Bull. Soc. Chim. Fr.* **1994**, *131*, 400–406, confirmed by K. Ikeda et al.[19] The assignment of the anomeric configuration was also supported by the values of the chemical shift difference between the two protons at C-3 and at C-4 $\Delta\delta$ {3-H–4-H}, which were around 0.3 ppm for α-glycosides, larger than suggested for β-glycosides. The assignment was also supported by a comparison of the chemical shift values of the proton at C-6, which was around 4.4 ppm for α-glycosides and around 4.0 ppm for β-glycosides.
[28] However, attempts to monitor or isolate possible N-glycoside intermediates by conducting the reaction of glycals **6a** or **6b** at lower temperature (23 °C) were unsuccessful.

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